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(21) International Application Number: PCT/US88/00222 (22) International Filing Date: 27 January 1988 (27.01.88) (31) Priority Application Numbers: 011,471 133,052 (32) Priority Dates: 30 January 1987 (30.01.87) 21 December 1987 (21.12.87) (33) Priority Country: US (71) Applicant: EXXON CHEMICAL PATENTS, INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US). (72) Inventors: TURNER, Howard, William ; 303 Elder Glen, Webster, TX 77598 (US). HLATKY, Gregory, George ; 15900 Space Center Boulevard, N-2, Hous- ton, TX 77062 (US).		(74) Agent: KURTZMAN, Myron, B.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522-5200 (US). (81) Designated States: AU, BR, DK, FI, HU, JP, KR, NO, SU. Published <i>With international search report.</i>
(54) Title: CATALYSTS, METHOD OF PREPARING THESE CATALYSTS, AND POLYMERIZATION PRO- CESSES WHEREIN THESE CATALYSTS ARE USED (57) Abstract A catalyst is prepared by combining a bis(cyclopentadienyl)zirconium compound with a second compound compris- ing a cation capable of donating a proton and a bulky, labile anion comprising a plurality of boron atoms capable of stabi- lizing the zirconium cation formally having a coordination number of 3 and a valence of +4 which is formed as a result of the combination. Many of the catalysts thus formed are stable and isolable and may be recovered and stored. The catalysts may be preformed and then used to polymerize olefins or the catalysts may be formed in situ during polymerization by ad- ding the separate components to the polymerization reaction. The catalyst will be formed when the two components are combined at a temperature within the range from about -100°C to about 300°C. The catalysts thus prepared afford better control of polymer molecular weight and are not subject to equilibrium reversal. The catalysts thus produced are also less pyrophoric than the more conventional Ziegler-Natta olefin polymerization catalysts.		

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CATALYSTS, METHOD OF PREPARING THESE CATALYSTS,
AND POLYMERIZATION PROCESSES WHEREIN THESE CATALY
STS ARE USED

1 This is a Continuation-in-Part of U. S. Patent Application
2 Serial No. 011,471, filed January 30, 1987.

3 BACKGROUND OF THE INVENTION

4 This invention relates to compositions of matter useful as
5 catalysts, to a method for preparing these catalysts, to a process
6 wherein these compositions of matter are used as catalysts and to
7 polymeric products produced with these catalysts. More
8 particularly, this invention relates to catalyst compositions, to a
9 method of making said catalyst compositions, to a method for
10 polymerizing olefins, diolefins and/or acetylenically unsaturated
11 monomers wherein these catalyst compositions are used, and to
12 polymeric products produced with these catalyst compositions.

13 The use of soluble Ziegler-Natta type catalysts in the
14 polymerization of olefins is, of course, well known in the prior
15 art. In general, these soluble systems comprise a Group IV-B metal
16 compound and a metal alkyl cocatalyst, particularly an aluminum
17 alkyl cocatalyst. A subgenus of these catalysts is that subgenus
18 comprising a bis(cyclopentadienyl) compound of the Group IV-B
19 metals, particularly titanium, and an aluminum alkyl cocatalyst.
20 While speculation remains concerning the actual structure of the
21 active catalyst species in this subgenus of soluble Ziegler-Natta
22 type olefin polymerization catalysts, it would appear generally
23 accepted that the active catalyst species is an ion or a
24 decomposition product thereof which will alkylate an olefin in the
25 presence of a labile stabilizing anion. This theory may have first
26 been advocated by Breslow and Newburg, and Long and Breslow, as
27 indicated in their respective articles appearing in J. Am. Chem.
28 Soc., 1959, Vol. 81, pp. 81-86, and J. Am. Chem. Soc., 1960, Vol.
29 82, pp. 1953-1957. As indicated in these articles, various studies
30 suggested that the active catalyst species is a titanium-alkyl
31 complex or a species derived therefrom when a titanium compound;
32 viz., bis(cyclopentadienyl)titanium dihalide, and an aluminum alkyl

1 are used as a catalyst or catalyst precursor. The presence of
2 ions, all being in equilibrium, when a titanium compound is used
3 was also suggested by Dyachkovskii, Vysokomol. Soyed., 1965, Vol.
4 7, pp. 114-115 and by Dyachkovskii, Shilova and Shilov, J. Polym.
5 Sci., Part C, 1967, pp. 2333-2339. That the active catalyst
6 species is a cation complex when a titanium compound is used, was
7 further suggested by Eisch et al., J. Am. Chem. Soc., 1985, Vol.
8 107, pp. 7219-7221.

9 While the foregoing articles teach or suggest that the
10 active catalyst species is an ion pair and, particularly an ion
11 pair wherein the metal component is present as a cation or a
12 decomposition product thereof, and while these references teach or
13 suggest coordination chemistry to form such active catalyst
14 species, all of the articles teach the use of a cocatalyst
15 comprising a Lewis acid either to form or to stabilize the active
16 ionic catalyst species. The active catalyst is, apparently, formed
17 through a Lewis acid-Lewis base reaction of two neutral components
18 (the metallocene and the aluminum alkyl), leading to an equilibrium
19 between a neutral, apparently inactive, adduct and an ion pair,
20 presumably the active catalyst. As a result of this equilibrium,
21 there is a competition for the anion which must be present to
22 stabilize the active cation catalyst species. This equilibrium is,
23 of course, reversible and such reversal will deactivate the
24 catalyst. Moreover, the catalyst systems heretofore contemplated
25 are subject to poisoning by the presence of basic impurities in the
26 system. Further, many, if not all, of the Lewis acids heretofore
27 contemplated for use in soluble Ziegler-Natta type catalyst systems
28 are chain transfer agents and, as a result, prevent effective
29 control of the product polymer molecular weight and product
30 molecular weight distribution. Still further, most, if not all, of
31 the cocatalysts heretofore contemplated are highly pyrophoric and,
32 as a result, somewhat hazardous to use.

33 The aforementioned catalyst systems have not, generally,
34 been particularly active when zirconium or hafnium is the Group
35 IV-B metal used. Recently, however, it has been found that active
36 Ziegler-Natta type catalysts can be formed when bis(cyclo-
37 pentadienyl)hafnium and bis(cyclopentadienyl)zirconium compounds

1 are used with alumoxanes. As is well known, these systems offer
2 several distinct advantages, including vastly higher catalytic
3 activities than the aforementioned bis (cyclopentadienyl)titanium
4 catalysts and the production of polymers with narrower molecular
5 weight distributions than those from conventional Ziegler-Natta
6 catalysts. These systems remain subject to poisoning when basic
7 impurities are present and do, however, require an undesirable
8 excess of the alumoxane to function efficiently. Moreover, the
9 hafnium containing systems are not as active as the zirconium
10 containing systems, at least when used for homopolymerization.
11 This has been suggested by Giannetti, Nicoletti, and Mazzocchi, J.
12 Polym. Sci., Polym. Chem., 1985, Vol. 23, pp. 2117-2133, who
13 claimed that the ethylene polymerization rates of bis(cyclo-
14 pentadienyl)hafnium compounds were five to ten times slower than
15 those of similar bis(cyclopentadienyl)zirconium compounds while
16 there was little difference between the two catalysts in the
17 molecular weight of the polyethylene formed from them.

18 In light of the several deficiencies of the coordination
19 catalyst systems heretofore contemplated, the need for an improved
20 coordination system which: (1) permits better control of molecular
21 weight and molecular weight distribution; (2) is not subject to
22 activation equilibrium; and (3) does not involve the use of an
23 undesirable cocatalyst is believed readily apparent.

24 SUMMARY OF THE INVENTION

25 It has now been discovered that the foregoing and other
26 disadvantages of the prior art ionic olefin polymerization
27 catalysts can be avoided, or at least reduced, with the ionic
28 catalysts of the present invention and an improved olefin, diolefin
29 and/or acetylenically unsaturated monomer polymerization process
30 provided therewith. It is, therefore, an object of this invention
31 to provide improved ionic catalyst systems useful in the
32 polymerization of olefins, diolefins and acetylenically unsaturated
33 monomers. It is another object of this invention to provide a
34 method for preparing such improved catalysts. It is a further
35 object of this invention to provide an improved polymerization
36 process using such improved catalysts. It is still another object
37 of this invention to provide such an improved catalyst which is not

1 subject to ion equilibrium reversal. It is still a further object
2 of this invention to provide such an improved catalyst which may
3 permit better control of the product polymer molecular weight and
4 molecular weight distribution. It is yet a further object of this
5 invention to provide such an improved catalyst which may be used
6 with less risk of fire. It is even another object of this
7 invention to provide polymeric products produced with these
8 improved catalysts having relatively narrow molecular weight
9 distributions and which are free of certain metal impurities. The
10 foregoing and still other objects and advantages of the present
11 invention will become apparent from the description set forth
12 hereinafter and the examples included herein.

13 In accordance with the present invention, the foregoing
14 and other objects and advantages are accomplished with and by using
15 a catalyst prepared by combining at least two components, the first
16 of which is a soluble, bis(cyclopentadienyl)-substituted Group IV-B
17 metal compound containing at least one ligand which will combine
18 with a Lewis or Bronsted acid thereby yielding a Group IV-B metal
19 cation and the second of which compounds comprises a cation capable
20 of donating a proton and reacting irreversibly with said ligand in
21 said Group IV-B metal compound to liberate a free, neutral
22 by-product and a compatible noncoordinating anion comprising a
23 plurality of boron atoms, which compatible noncoordinating anion is
24 stable, bulky and labile. The soluble Group IV-B metal compound
25 must be capable of forming a cation formally having a coordination
26 number of 3 and a valence of +4 when said ligand is liberated
27 therefrom. The anion of the second compound must be capable of
28 stabilizing the Group IV-B metal cation complex without interfering
29 with the Group IV-B metal cation's or its decomposition product's
30 ability to function as a catalyst and must be sufficiently labile
31 to permit displacement by an olefin, a diolefin or an
32 acetylenically unsaturated monomer during polymerization. For
33 example, Bochmann and Wilson have reported (J. Chem. Soc., Chem.
34 Comm., 1986, pp. 1610-1611) that bis(cyclopentadienyl)-titanium
35 dimethyl reacts with tetrafluoroboric acid to form bis(cyclo-
36 pentadienyl)titanium methyl tetrafluoroborate. The anion is,
37 however, insufficiently labile to be displaced by ethylene.

1 DETAILED DESCRIPTION OF THE INVENTION

2 As indicated supra, the present invention relates to
3 catalysts, to a method for preparing such catalysts, to a method of
4 using such catalysts and to polymeric products produced with such
5 catalysts. The catalysts are particularly useful in the
6 polymerization of α -olefins, diolefins and acetylenically
7 unsaturated monomers. The improved catalysts are prepared by
8 combining at least one first compound which is a bis(cyclo-
9 pentadienyl) derivative of a metal of Group IV-B of the Periodic
10 Table of the Elements capable of forming a cation formally having a
11 coordination number of 3 and a valence of +4 and at least one
12 second compound comprising a cation capable of donating a proton
13 and a compatible noncoordinating anion comprising a plurality of
14 boron atoms, which anion is both bulky and labile, and capable of
15 stabilizing the Group IV-B metal cation without interfering with
16 said Group IV-B metal cation's or its decomposition product's
17 ability to polymerize α -olefins, diolefins and/or acetylenically
18 unsaturated monomers.

19 All reference to the Periodic Table of the Elements herein
20 shall refer to the Periodic Table of the Elements, as published and
21 copyrighted by CRC Press, Inc., 1984. Also, any reference to a
22 Group or Groups of such Periodic Table of the Elements shall be to
23 the Group or Groups as reflected in this Periodic Table of the
24 Elements.

25 As used herein, the recitation "compatible noncoordinating
26 anion" means an anion which either does not coordinate to said
27 cation or which is only weakly coordinated to said cation thereby
28 remaining sufficiently labile to be displaced by a neutral Lewis
29 base. The recitation "compatible noncoordinating anion"
30 specifically refers to an anion which when functioning as a
31 stabilizing anion in the catalyst system of this invention does not
32 transfer an anionic substituent or fragment thereof to said cation
33 thereby forming a neutral four coordinate metallocene and a neutral
34 boron by-product. Compatible anions are those which are not
35 degraded to neutrality when the initially formed complex decomposes.

36 The Group IV-B metal compounds, and particularly titanium,
37 zirconium and hafnium compounds, useful as first compounds in the

1 improved catalyst of this invention are bis(cyclopentadienyl)
 2 derivatives of titanium, zirconium and hafnium. In general, useful
 3 titanium, zirconium and hafnium compounds may be represented by the
 4 following general formulae:

- 5 1. $(A-Cp)MX_1X_2$
- 6 2. $(A-Cp)MX'_1X'_2$
- 7 3. $(A-Cp)ML$
- 8 4. $(Cp^*)(CpR)MX_1$

9 Wherein:

10 M is a metal selected from the Group consisting of
 11 titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is
 12 either $(Cp)(Cp^*)$ or $Cp-A'-Cp^*$ and Cp and Cp^* are the
 13 same or different substituted or unsubstituted cyclo-
 14 pentadienyl radicals, wherein A' is a covalent bridging
 15 group containing a Group IV-A element; L is an olefin,
 16 diolefin or aryne ligand; X_1 and X_2 are,
 17 independently, selected from the Group consisting of
 18 hydride radicals, hydrocarbyl radicals having from 1 to
 19 about 20 carbon atoms, substituted-hydrocarbyl radicals,
 20 wherein 1 or more of the hydrogen atoms are replaced with
 21 a halogen atom, having from 1 to about 20 carbon atoms,
 22 organo-metalloid radicals comprising a Group IV-A element
 23 wherein each of the hydrocarbyl substituents contained in
 24 the organo portion of said organo-metalloid,
 25 independently, contain from 1 to about 20 carbon atoms and
 26 the like; X'_1 and X'_2 are joined and bound to the
 27 metal atom to form a metallacycle, in which the metal,
 28 X'_1 and X'_2 form a hydrocarbocyclic ring containing
 29 from about 3 to about 20 carbon atoms; and R is a
 30 substituent, preferably a hydrocarbyl substituent, having
 31 from 1 to about 20 carbon atoms, on one of the
 32 cyclopentadienyl radicals which is also bound to the metal
 33 atom.

34 Each carbon atom in the cyclopentadienyl radical may be,
 35 independently, unsubstituted or substituted with the same or a
 36 different radical selected from the Group consisting of hydrocarbyl
 37 radicals, substituted-hydrocarbyl radicals wherein one or more

1 hydrogen atoms is replaced by a halogen atom, hydrocarbyl-
2 substituted metalloids wherein the metalloid is selected
3 from Group IV-A of the Periodic Table of the Elements, halogen
4 radicals and the like. Suitable hydrocarbyl and substituted-
5 hydrocarbyl radicals which may be substituted for at least one
6 hydrogen atom in the cyclopentadienyl radical will contain from 1
7 to about 20 carbon atoms and include straight and branched alkyl
8 radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic
9 hydrocarbon radicals, aromatic radicals and alkyl-substituted
10 aromatic radicals. Similarly, and when X_1 and/or X_2 is a
11 hydrocarbyl or substituted-hydrocarbyl radical, each may,
12 independently, contain from 1 to about 20 carbon atoms and be a
13 straight or branched alkyl radical, a cyclic hydrocarbyl radical,
14 an alkyl-substituted cyclic hydrocarbyl radical, an aromatic
15 radical or an alkyl-substituted aromatic radical. Suitable
16 organo-metalloid radicals include mono-, di- and trisubstituted
17 organo-metalloid radicals of Group IV-A elements wherein each of
18 the hydrocarbyl Groups contains from 1 to about 20 carbon atoms.
19 Suitable organo-metalloid radicals include trimethylsilyl, tri-
20 ethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenyl-
21 germyl, trimethylgermyl and the like.

22 Illustrative, but not limiting examples of bis(cyclo-
23 pentadienyl)zirconium compounds which may be used in the
24 preparation of the improved catalyst of this invention are
25 dihydrocarbyl-substituted bis(cyclopentadienyl)zirconium compounds
26 such as bis(cyclopentadienyl)zirconium dimethyl,
27 bis(cyclopentadienyl)zirconium diethyl, bis(cyclopentadienyl)
28 zirconium dipropyl, bis(cyclopentadienyl)zirconium dibutyl,
29 bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)
30 zirconium dineopentyl, bis(cyclopentadienyl)zirconium di(m-tolyl),
31 bis(cyclopentadienyl)zirconium di(p-tolyl) and the like;
32 (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds
33 such as (methylcyclopentadienyl)(cyclopentadienyl) and
34 bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclo-
35 pentadienyl)(cyclopentadienyl) and bis(ethylcyclopentadienyl)
36 zirconium dimethyl, (propylcyclopentadienyl)(cyclopentadienyl) and
37 bis(propylcyclopentadienyl)zirconium dimethyl, (n-butylcyclo-

1 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)
2 zirconium dimethyl, (t-butylcyclopentadienyl)(cyclopentadienyl) and
3 bis(t-butylcyclopentadienyl)zirconium dimethyl, (cyclohexylmethyl-
4 cyclopentadienyl)(cyclopentadienyl) and bis(cyclohexylmethylcyclo-
5 pentadienyl)zirconium dimethyl, (benzylcyclopentadienyl)
6 (cyclopentadienyl) and bis(benzylcyclopentadienyl)zirconium
7 dimethyl, (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and
8 bis(diphenylmethylcyclopentadienyl)zirconium dimethyl,
9 (methylcyclopentadienyl)(cyclopentadienyl) and bis(methylcyclo-
10 pentadienyl)zirconium dihydride, (ethylcyclopenta dienyl)
11 (cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium
12 dihydride, (propylcyclopentadienyl)(cyclopentadienyl) and
13 bis(propylcyclopentadienyl)zirconium dihydride, (n-butylcyclo-
14 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)
15 zirconium dihydride, (t-butylcyclopentadienyl)(cyclopentadienyl)
16 and bis(t-butylcyclopentadienyl)zirconium dihydride,
17 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and
18 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
19 (benzylcyclopentadienyl)(cyclopentadienyl) and bis(benzyl-
20 cyclopentadienyl)zirconium dihydride, (diphenylmethylcyclo-
21 pentadienyl)(cyclopentadienyl) and bis(diphenylmethylcyclopenta-
22 dienyl)zirconium dihydride and the like; (polyhydrocarbyl-
23 substituted-cyclopentadienyl)zirconium compounds such as
24 (dimethylcyclopentadienyl)(cyclopentadienyl) and bis(dimethylcyclo-
25 pentadienyl)zirconium dimethyl, (trimethylcyclopentadienyl)
26 (cyclopentadienyl) and bis(trimethylcyclopentadienyl)zirconium
27 dimethyl, (tetramethylcyclopentadienyl)(cyclopentadienyl) and
28 bis(tetramethylcyclopentadienyl)zirconium dimethyl,
29 (permethylcyclopentadienyl)(cyclopentadienyl) and bis(permethyl-
30 cyclopentadienyl)zirconium dimethyl, (ethyltetramethylcyclopenta-
31 dienyl)(cyclopentadienyl) and bis(ethyltetramethylcyclopentadienyl)
32 zirconium dimethyl, (indenyl)(cyclopentadienyl) and bis(indenyl)
33 zirconium dimethyl, (dimethylcyclopentadienyl)(cyclopentadienyl)
34 and bis(dimethylcyclopentadienyl)zirconium dihydride,
35 (trimethylcyclopentadienyl)(cyclopentadienyl) and bis(trimethyl-
36 cyclopentadienyl)zirconium dihydride, (tetramethylcyclopenta-
37 dienyl) (cyclopentadienyl) and bis(tetramethylcyclo-

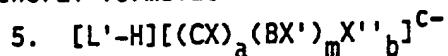
1 pentadienyl)zirconium dihydride, (permethylcyclopentadienyl)
2 (cyclopentadienyl) and bis(permethylcyclopentadienyl)zirconium
3 dihydride, (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and
4 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
5 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride and
6 the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium
7 compounds such as (trimethylsilylcyclopentadienyl)(cyclopenta-
8 dienyl) and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,
9 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and bis(tri-
10 methylgermylcyclopentadienyl)zirconium dimethyl, (trimethyl-
11 stannylcyclopentadienyl)(cyclopentadienyl) and
12 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,
13 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
14 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,
15 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and
16 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,
17 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
18 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,
19 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
20 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,
21 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
22 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the
23 like; (halogen-substituted-cyclopentadienyl)zirconium compounds
24 such as (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
25 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl,
26 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
27 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the
28 like; silyl-substituted bis(cyclopentadienyl)zirconium compounds
29 such as bis(cyclopentadienyl)(trimethylsilyl)(methyl)zirconium,
30 bis(cyclopentadienyl)(triphenylsilyl)(methyl)zirconium,
31 bis(cyclopentadienyl)[tris(dimethylsilyl)silyl](methyl)zirconium,
32 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,
33 bis(cyclopentadienyl)(trimethylsilyl)(trimethylsilylmethyl)zirconium,
34 bis(cyclopentadienyl)(trimethylsilyl)(benzyl) and the like;
35 (bridged-cyclopentadienyl)zirconium compounds such as methylene
36 bis(cyclopentadienyl)zirconium dimethyl, ethylene
37 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl

1 bis(cyclopentadienyl)zirconium dimethyl, methylene bis(cyclopentad-
2 ienyl)zirconium dihydride, ethylene bis(cyclopentadienyl)zirconium
3 dihydride and dimethylsilyl bis(cyclopentadienyl)zirconium
4 dihydride and the like; zirconacycles such as bis(pentamethylcyclo-
5 pentadienyl) zirconacyclobutane, bis(pentamethylcyclopentadienyl)
6 zirconacyclopentane, bis(cyclopentadienyl)zirconaindane and the
7 like; olefin, diolefin and aryne ligand substituted bis(cyclop-
8 entadienyl)zirconium compounds such as bis(cyclopentadienyl)
9 (1,3-butadiene)zirconium, bis(cyclopentadienyl) (2,3-dimethyl-1,3-
10 butadiene)zirconium, bis(pentamethylcyclopentadienyl)(benzyne)
11 zirconium and the like; (hydrocarbyl)(hydride) bis(cyclopenta-
12 dienyl)zirconium compounds such as bis(pentamethylcyclopenta-
13 dienyl)zirconium (phenyl)(hydride), bis(pentamethylcyclopenta-
14 dienyl)zirconium (methyl)(hydride) and the like; and bis(cyclo-
15 pentadienyl)zirconium compounds in which a substituent on the
16 cyclopentadienyl radical is bound to the metal such as
17 (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylene)
18 zirconium hydride, (pentamethylcyclopentadienyl)(tetramethylcyclo-
19 pentadienylmethylene) zirconium phenyl and the like.

20 A similar list of illustrative bis(cyclopentadienyl)
21 hafnium and bis(cyclopentadienyl)titanium compounds could be made,
22 but since the lists would be nearly identical to that already
23 presented with respect to bis(cyclopentadienyl)zirconium compounds,
24 such lists are not deemed essential to a complete disclosure.
25 Those skilled in the art, however, are aware that bis(cyclo-
26 pentadienyl)hafnium compounds and bis(cyclopentadienyl) titanium
27 compounds corresponding to certain of the bis(cyclopentadienyl)
28 zirconium compounds listed supra are not known. The lists would,
29 therefore, be reduced by these compounds. Other bis(cyclopenta-
30 dienyl)hafnium compounds and other bis(cyclopentadienyl)titanium
31 compounds as well as other bis(cyclopentadienyl)zirconium compounds
32 which are useful in the catalyst compositions of this invention
33 will, of course, be apparent to those skilled in the art.

34 Compounds useful as a second component in the preparation
35 of the catalyst of this invention will comprise a cation, which is
36 a Bronsted acid capable of donating a proton, and a compatible

1 anion containing a plurality of boron atoms, which anion is
 2 relatively large, capable of stabilizing the active catalyst
 3 species which is formed when the two compounds are combined and
 4 said anion will be sufficiently labile to be displaced by olefinic,
 5 diolefinic and acetylenically unsaturated substrates or other
 6 neutral Lewis bases such as ethers, nitriles and the like. In
 7 general, a second compound useful in the preparation of the
 8 catalysts of this invention may be any compound represented by one
 9 of the following general formulae:



11 Wherein:

12 L'-H is either H⁺, ammonium or a substituted ammonium
 13 cation having up to 3 hydrogen atoms replaced with a
 14 hydrocarbyl radical containing from 1 to about 20 carbon
 15 atoms or a substituted-hydrocarbyl radical, wherein one or
 16 more of the hydrogen atoms is replaced by a halogen atom,
 17 containing from 1 to about 20 carbon atoms, phosphonium
 18 radicals, substituted-phosphonium radicals having up to 3
 19 hydrogen atoms replaced with a hydrocarbyl radical
 20 containing from 1 to about 20 carbon atoms or a
 21 substituted-hydrocarbyl radical, wherein 1 or more of the
 22 hydrogen atoms is replaced by a halogen atom, containing
 23 from 1 to about 20 carbon atoms and the like; B and C are,
 24 respectively, boron and carbon; X, X' and X'' are radicals
 25 selected, independently, from the Group consisting of
 26 hydride radicals, halide radicals, hydrocarbyl radicals
 27 containing from 1 to about 20 carbon atoms,
 28 substituted-hydrocarbyl radicals, wherein one or more of
 29 the hydrogen atoms is replaced by a halogen atom,
 30 containing from 1 to about 20 carbon atoms, organo-
 31 metalloid radicals wherein each hydrocarbyl substitution
 32 in the organo portion contains from 1 to about 20 carbon
 33 atoms and said metal is selected from Group IV-A of the
 34 Periodic Table of the Elements and the like; a and b are
 35 integers ≥ 0 ; c is an integer ≥ 1 ; a + b + c = an
 36 even-numbered integer from 2 to about 8; and m is an
 37 integer ranging from 5 to about 22.

1 6. $[L'-H][[(CX_3)_a, (BX_4)_m, (X_5)_b,]^{c'}]_2^{n+}]^{d-}$

2 Wherein:

3 $L'-H$ is either H^+ , ammonium or a substituted ammonium
 4 radical having up to 3 hydrogen atoms replaced with a
 5 hydrocarbyl radical containing from 1 to about 20 carbon
 6 atoms or a substituted-hydrocarbyl radical, wherein 1 or
 7 more of the hydrogen atoms is replaced by a halogen atom,
 8 containing from 1 to about 20 carbon atoms, a phosphonium
 9 radical, a substituted-phosphonium radical having up to 3
 10 hydrogen atoms replaced with a hydrocarbyl radical
 11 containing from 1 to about 20 carbon atoms or a
 12 substituted-hydrocarbyl radical, wherein 1 or more of the
 13 hydrogen atoms is replaced by a halogen atom, containing
 14 from 1 to about 20 carbon atoms and the like; B, C, M and
 14 H are, respectively, boron; carbon, a transition metal and
 15 hydrogen; X_3 , X_4 , and X_5 are radicals selected,
 16 independently, from the Group consisting of hydride
 17 radicals, halide radicals, hydrocarbyl radicals containing
 18 from 1 to about 20 carbon atoms, substituted-hydrocarbyl
 19 radicals, wherein one or more of the hydrogen atoms is
 20 replaced by a halogen atom, containing from 1 to about 20
 21 carbon atoms, organo-metalloid radicals wherein each
 22 hydrocarbyl substitution in the organo portion or said
 23 organo-metalloid contains from 1 to about 20 carbon atoms
 24 and said metal is selected from Group IV-A of the Periodic
 25 Table of the Elements and the like; a' and b' are the same
 26 or a different integer ≥ 0 ; c' is an integer ≥ 2 ;
 27 $a' + b' + c' =$ an even-numbered integer from 4 to about 8;
 28 m' is an integer from 6 to about 12; n is an integer such
 29 that $2c' - n = d$; and d is an integer ≥ 1 .

30 Illustrative, but not limiting, examples of the second
 31 compounds which can be used as a second component in the catalyst
 32 compositions of this invention are ammonium salts such as ammonium
 33 1-carbadodecaborate (using 1-carbadodecaborate as an illustrative,
 34 but not limiting, counterion for the ammonium cations listed
 35 below): monohydrocarbyl-substituted ammonium salts such as
 36 methylammonium 1-carbadodecaborate, ethylammonium 1-carbadode-

1 caborate, propylammonium 1-carbadodecaborate, isopropylammonium
 2 1-carbadodecaborate, (n-butyl)ammonium 1-carbadodecaborate,
 3 anilinium 1-carbadodecaborate, and (p-tolyl)ammonium
 4 1-carbadodecaborate and the like; dihydrocarbyl-substituted
 5 ammonium salts such as dimethylammonium 1-carbadodecaborate,
 6 diethylammonium 1-carbadodecaborate, dipropylammonium
 7 1-carbadodecaborate, diisopropylammonium 1-carbadodecaborate,
 8 di(n-butyl)ammonium 1-carbadodecaborate, diphenylammonium
 9 1-carbadodecaborate, di(p-tolyl)ammonium 1-carbadodecaborate and
 10 the like; trihydrocarbyl-substituted ammonium salts such as
 11 trimethylammonium 1-carbadodecaborate, triethylammonium
 12 1-carbadodecaborate, tripropylammonium 1-carbadodecaborate,
 13 tri(n-butyl) ammonium 1-carbadodecaborate, triphenylammonium
 14 1-carbadodecaborate, tri(p-tolyl)ammonium 1-carbadodecaborate,
 15 N,N-dimethylanilinium 1-carbadodecaborate, N,N-diethylanilinium
 16 1-carbadodecaborate and the like.

17 Illustrative, but not limiting examples of second
 18 compounds corresponding to Formula 5 [using tri(n-butyl)ammonium as
 19 an illustrative, but not limiting, counterion for the anions listed
 20 below] are salts of anions such as bis[tri(n-butyl)ammonium]
 21 nonaborate, bis[tri(n-butyl)ammonium]decaborate,
 22 bis[tri(n-butyl)ammonium]undecaborate, bis[tri(n-butyl)ammonium]
 23 dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate,
 24 bis[tri(n-butyl)ammonium]dodecachlorododecaborate,
 25 tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium
 26 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate,
 27 tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate,
 28 tri(n-butyl)ammonium dibromo-1-carbadodecaborate and the like;
 29 borane and carborane complexes and salts of borane and carborane
 30 anions such as decaborane(14), 7,8-dicarbaundecaborane(13),
 31 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-
 32 dicarbaundecaborane, dodecahydrido-11-methyl-2,7-di-
 33 carbaundecaborane, tri(n-butyl)ammonium undecaborate(14),
 34 tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium
 35 7-carbaundecaborate(13), tri(n-butyl)ammonium 7,8-dicarbaunde-
 36 caborate(12), tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),
 37 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaunde-

1 caborate, tri(n-butyl)ammonium undecahydrido-8-ethyl-
2 7,9-dicarbaundecaborate, tri(n-butyl)ammonium undecahydrido-
3 8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium
4 undecahydrido-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium
5 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,
6 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate
7 and the like; boranes and carboranes and salts of boranes and
8 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanona-
9 borane(13), 6,9-dicarbadeceborane(14), dodecahydrido-1-
10 phenyl-1,3-dicarbanonaborane, dodecahydrido-1-methyl-1,3-
11 dicarbanonaborane, undecahydrido-1,3-dimethyl-1,3-dicarbanona-
12 borane and the like.

13 Illustrative, but not limiting, examples of second
14 compounds corresponding to Formula 6 [using tri(n-butyl)ammonium as
15 an illustrative, but not limiting, counterion for the anions listed
16 below] are salts of metallocarborane and metallocaborane anions such
17 as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)
18 cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-
19 dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undeca-
20 hydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)
21 ammonium bis(undecahydrido-7,8-dicarbaundecaborato)nickelate(III),
22 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)
23 cuprate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicar-
24 baundecaborato)aurate(III), tri(n-butyl)ammonium bis(nonahydrido-
25 7,8-dimethyl-7,8-dicarbaundecaborato)-ferrate(III), tri(n-butyl)
26 ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)
27 chromate(III), tri(n-butyl)ammonium bis(tribromooctahydrido-
28 7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium
29 bis(dodecahydridodicarbadeceborato)cobaltate(III),
30 bis[tri(n-butyl)ammonium] bis(dodecahydridodecaborato)
31 nickelate(II), tris[tri(n-butyl)ammonium] bis(undecahydrido-7-
32 carbaundecaborato)chromate(III), bis[tri(n-butyl) ammonium]
33 bis(undecahydrido-7-carbaundecaborato)manganate(IV),
34 bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)
35 cobaltate(III), bis[tri(n-butyl)ammonium] bis(undecahydrido-7-
36 carbaundecaborato)nickelate(IV) and the like. A similar list of
37 representative phosphonium compounds could be recited as

1 illustrative second compounds, but for the sake of brevity, it is
2 simply noted that the phosphonium and substituted-phosphonium salts
3 corresponding to the listed ammonium and substituted-ammonium salts
4 could be used as second compounds in the present invention.

5 In general, and while most first components identified
6 above may be combined with most second components identified above
7 to produce an active olefin polymerization catalyst, it is
8 important to continued polymerization operations that either the
9 initially formed metal cation or a decomposition product thereof be
10 a relatively stable olefin polymerization catalyst. It is also



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(54) Title: CATALYSTS, METHOD OF PREPARING THESE CATALYSTS, AND POLYMERIZATION PRO- CESSES WHEREIN THESE CATALYSTS ARE USED (57) Abstract A catalyst is prepared by combining a bis(cyclopentadienyl)zirconium compound with a second compound compris- ing a cation capable of donating a proton and a bulky, labile anion comprising a plurality of boron atoms capable of stabi- lizing the zirconium cation formally having a coordination number of 3 and a valence of +4 which is formed as a result of the combination. Many of the catalysts thus formed are stable and isolable and may be recovered and stored. The catalysts may be preformed and then used to polymerize olefins or the catalysts may be formed in situ during polymerization by ad- ding the separate components to the polymerization reaction. The catalyst will be formed when the two components are combined at a temperature within the range from about -100°C to about 300°C. The catalysts thus prepared afford better control of polymer molecular weight and are not subject to equilibrium reversal. The catalysts thus produced are also less pyrophoric than the more conventional Ziegler-Natta olefin polymerization catalysts.		

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CATALYSTS, METHOD OF PREPARING THESE CATALYSTS,
AND POLYMERIZATION PROCESSES WHEREIN THESE CATALYSTS ARE USED

This is a Continuation-in-Part of U. S. Patent Application
Serial No. 011,471, filed January 30, 1987.

BACKGROUND OF THE INVENTION

This invention relates to compositions of matter useful as catalysts, to a method for preparing these catalysts, to a process wherein these compositions of matter are used as catalysts and to polymeric products produced with these catalysts. More particularly, this invention relates to catalyst compositions, to a method of making said catalyst compositions, to a method for polymerizing olefins, diolefins and/or acetylenically unsaturated monomers wherein these catalyst compositions are used, and to polymeric products produced with these catalyst compositions.

The use of soluble Ziegler-Natta type catalysts in the polymerization of olefins is, of course, well known in the prior art. In general, these soluble systems comprise a Group IV-B metal compound and a metal alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. A subgenus of these catalysts is that subgenus comprising a bis(cyclopentadienyl) compound of the Group IV-B metals, particularly titanium, and an aluminum alkyl cocatalyst. While speculation remains concerning the actual structure of the active catalyst species in this subgenus of soluble Ziegler-Natta type olefin polymerization catalysts, it would appear generally accepted that the active catalyst species is an ion or a decomposition product thereof which will alkylate an olefin in the presence of a labile stabilizing anion. This theory may have first been advocated by Breslow and Newburg, and Long and Breslow, as indicated in their respective articles appearing in J. Am. Chem. Soc., 1959, Vol. 81, pp. 81-86, and J. Am. Chem. Soc., 1960, Vol. 82, pp. 1953-1957. As indicated in these articles, various studies suggested that the active catalyst species is a titanium-alkyl complex or a species derived therefrom when a titanium compound; viz., bis(cyclopentadienyl)titanium dihalide, and an aluminum alkyl

1 are used as a catalyst or catalyst precursor. The presence of
2 ions, all being in equilibrium, when a titanium compound is used
3 was also suggested by Dyachkovskii, Vysokomol. Soyed., 1965, Vol.
4 7, pp. 114-115 and by Dyachkovskii, Shilova and Shilov, J. Polym.
5 Sci., Part C, 1967, pp. 2333-2339. That the active catalyst
6 species is a cation complex when a titanium compound is used, was
7 further suggested by Eisch et al., J. Am. Chem. Soc., 1985, Vol.
8 107, pp. 7219-7221.

9 While the foregoing articles teach or suggest that the
10 active catalyst species is an ion pair and, particularly an ion
11 pair wherein the metal component is present as a cation or a
12 decomposition product thereof, and while these references teach or
13 suggest coordination chemistry to form such active catalyst
14 species, all of the articles teach the use of a cocatalyst
15 comprising a Lewis acid either to form or to stabilize the active
16 ionic catalyst species. The active catalyst is, apparently, formed
17 through a Lewis acid-Lewis base reaction of two neutral components
18 (the metallocene and the aluminum alkyl), leading to an equilibrium
19 between a neutral, apparently inactive, adduct and an ion pair,
20 presumably the active catalyst. As a result of this equilibrium,
21 there is a competition for the anion which must be present to
22 stabilize the active cation catalyst species. This equilibrium is,
23 of course, reversible and such reversal will deactivate the
24 catalyst. Moreover, the catalyst systems heretofore contemplated
25 are subject to poisoning by the presence of basic impurities in the
26 system. Further, many, if not all, of the Lewis acids heretofore
27 contemplated for use in soluble Ziegler-Natta type catalyst systems
28 are chain transfer agents and, as a result, prevent effective
29 control of the product polymer molecular weight and product
30 molecular weight distribution. Still further, most, if not all, of
31 the cocatalysts heretofore contemplated are highly pyrophoric and,
32 as a result, somewhat hazardous to use.

33 The aforementioned catalyst systems have not, generally,
34 been particularly active when zirconium or hafnium is the Group
35 IV-B metal used. Recently, however, it has been found that active
36 Ziegler-Natta type catalysts can be formed when bis(cyclo-
37 pentadienyl)hafnium and bis(cyclopentadienyl)zirconium compounds

1 are used with alumoxanes. As is well known, these systems offer
2 several distinct advantages, including vastly higher catalytic
3 activities than the aforementioned bis (cyclopentadienyl)titanium
4 catalysts and the production of polymers with narrower molecular
5 weight distributions than those from conventional Ziegler-Natta
6 catalysts. These systems remain subject to poisoning when basic
7 impurities are present and do, however, require an undesirable
8 excess of the alumoxane to function efficiently. Moreover, the
9 hafnium containing systems are not as active as the zirconium
10 containing systems, at least when used for homopolymerization.
11 This has been suggested by Giannetti, Nicoletti, and Mazzocchi, J.
12 Polym. Sci., Polym. Chem., 1985, Vol. 23, pp. 2117-2133, who
13 claimed that the ethylene polymerization rates of bis(cyclo-
14 pentadienyl)hafnium compounds were five to ten times slower than
15 those of similar bis(cyclopentadienyl)zirconium compounds while
16 there was little difference between the two catalysts in the
17 molecular weight of the polyethylene formed from them.

18 In light of the several deficiencies of the coordination
19 catalyst systems heretofore contemplated, the need for an improved
20 coordination system which: (1) permits better control of molecular
21 weight and molecular weight distribution; (2) is not subject to
22 activation equilibrium; and (3) does not involve the use of an
23 undesirable cocatalyst is believed readily apparent.

24 SUMMARY OF THE INVENTION

25 It has now been discovered that the foregoing and other
26 disadvantages of the prior art ionic olefin polymerization
27 catalysts can be avoided, or at least reduced, with the ionic
28 catalysts of the present invention and an improved olefin, diolefin
29 and/or acetylenically unsaturated monomer polymerization process
30 provided therewith. It is, therefore, an object of this invention
31 to provide improved ionic catalyst systems useful in the
32 polymerization of olefins, diolefins and acetylenically unsaturated
33 monomers. It is another object of this invention to provide a
34 method for preparing such improved catalysts. It is a further
35 object of this invention to provide an improved polymerization
36 process using such improved catalysts. It is still another object
37 of this invention to provide such an improved catalyst which is not

1 subject to ion equilibrium reversal. It is still a further object
2 of this invention to provide such an improved catalyst which may
3 permit better control of the product polymer molecular weight and
4 molecular weight distribution. It is yet a further object of this
5 invention to provide such an improved catalyst which may be used
6 with less risk of fire. It is even another object of this
7 invention to provide polymeric products produced with these
8 improved catalysts having relatively narrow molecular weight
9 distributions and which are free of certain metal impurities. The
10 foregoing and still other objects and advantages of the present
11 invention will become apparent from the description set forth
12 hereinafter and the examples included herein.

13 In accordance with the present invention, the foregoing
14 and other objects and advantages are accomplished with and by using
15 a catalyst prepared by combining at least two components, the first
16 of which is a soluble, bis(cyclopentadienyl)-substituted Group IV-B
17 metal compound containing at least one ligand which will combine
18 with a Lewis or Bronsted acid thereby yielding a Group IV-B metal
19 cation and the second of which compounds comprises a cation capable
20 of donating a proton and reacting irreversibly with said ligand in
21 said Group IV-B metal compound to liberate a free, neutral
22 by-product and a compatible noncoordinating anion comprising a
23 plurality of boron atoms, which compatible noncoordinating anion is
24 stable, bulky and labile. The soluble Group IV-B metal compound
25 must be capable of forming a cation formally having a coordination
26 number of 3 and a valence of +4 when said ligand is liberated
27 therefrom. The anion of the second compound must be capable of
28 stabilizing the Group IV-B metal cation complex without interfering
29 with the Group IV-B metal cation's or its decomposition product's
30 ability to function as a catalyst and must be sufficiently labile
31 to permit displacement by an olefin, a diolefin or an
32 acetylenically unsaturated monomer during polymerization. For
33 example, Bochmann and Wilson have reported (J. Chem. Soc., Chem.
34 Comm., 1986, pp. 1610-1611) that bis(cyclopentadienyl)-titanium
35 dimethyl reacts with tetrafluoroboric acid to form bis(cyclo-
36 pentadienyl)titanium methyl tetrafluoroborate. The anion is,
37 however, insufficiently labile to be displaced by ethylene.

1 DETAILED DESCRIPTION OF THE INVENTION

2 As indicated supra, the present invention relates to
3 catalysts, to a method for preparing such catalysts, to a method of
4 using such catalysts and to polymeric products produced with such
5 catalysts. The catalysts are particularly useful in the
6 polymerization of α -olefins, diolefins and acetylenically
7 unsaturated monomers. The improved catalysts are prepared by
8 combining at least one first compound which is a bis(cyclo-
9 pentadienyl) derivative of a metal of Group IV-B of the Periodic
10 Table of the Elements capable of forming a cation formally having a
11 coordination number of 3 and a valence of +4 and at least one
12 second compound comprising a cation capable of donating a proton
13 and a compatible noncoordinating anion comprising a plurality of
14 boron atoms, which anion is both bulky and labile, and capable of
15 stabilizing the Group IV-B metal cation without interfering with
16 said Group IV-B metal cation's or its decomposition product's
17 ability to polymerize α -olefins, diolefins and/or acetylenically
18 unsaturated monomers.

19 All reference to the Periodic Table of the Elements herein
20 shall refer to the Periodic Table of the Elements, as published and
21 copyrighted by CRC Press, Inc., 1984. Also, any reference to a
22 Group or Groups of such Periodic Table of the Elements shall be to
23 the Group or Groups as reflected in this Periodic Table of the
24 Elements.

25 As used herein, the recitation "compatible noncoordinating
26 anion" means an anion which either does not coordinate to said
27 cation or which is only weakly coordinated to said cation thereby
28 remaining sufficiently labile to be displaced by a neutral Lewis
29 base. The recitation "compatible noncoordinating anion"
30 specifically refers to an anion which when functioning as a
31 stabilizing anion in the catalyst system of this invention does not
32 transfer an anionic substituent or fragment thereof to said cation
33 thereby forming a neutral four coordinate metallocene and a neutral
34 boron by-product. Compatible anions are those which are not
35 degraded to neutrality when the initially formed complex decomposes.
36 The Group IV-B metal compounds, and particularly titanium,
37 zirconium and hafnium compounds, useful as first compounds in the

1 improved catalyst of this invention are bis(cyclopentadienyl)
 2 derivatives of titanium, zirconium and hafnium. In general, useful
 3 titanium, zirconium and hafnium compounds may be represented by the
 4 following general formulae:

- 5 1. $(A-Cp)MX_1X_2$
- 6 2. $(A-Cp)MX'_1\overline{X'_2}$
- 7 3. $(A-Cp)ML$
- 8 4. $(Cp^*)(CpR)\overline{MX_1}$

9 Wherein:

10 M is a metal selected from the Group consisting of
 11 titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is
 12 either $(Cp)(Cp^*)$ or $Cp-A'-Cp^*$ and Cp and Cp^* are the
 13 same or different substituted or unsubstituted cyclo-
 14 pentadienyl radicals, wherein A' is a covalent bridging
 15 group containing a Group IV-A element; L is an olefin,
 16 diolefin or aryne ligand; X_1 and X_2 are,
 17 independently, selected from the Group consisting of
 18 hydride radicals, hydrocarbyl radicals having from 1 to
 19 about 20 carbon atoms, substituted-hydrocarbyl radicals,
 20 wherein 1 or more of the hydrogen atoms are replaced with
 21 a halogen atom, having from 1 to about 20 carbon atoms,
 22 organo-metalloid radicals comprising a Group IV-A element
 23 wherein each of the hydrocarbyl substituents contained in
 24 the organo portion of said organo-metalloid,
 25 independently, contain from 1 to about 20 carbon atoms and
 26 the like; X'_1 and X'_2 are joined and bound to the
 27 metal atom to form a metallacycle, in which the metal,
 28 X'_1 and X'_2 form a hydrocarbocyclic ring containing
 29 from about 3 to about 20 carbon atoms; and R is a
 30 substituent, preferably a hydrocarbyl substituent, having
 31 from 1 to about 20 carbon atoms, on one of the
 32 cyclopentadienyl radicals which is also bound to the metal
 33 atom.

34 Each carbon atom in the cyclopentadienyl radical may be,
 35 independently, unsubstituted or substituted with the same or a
 36 different radical selected from the Group consisting of hydrocarbyl
 37 radicals, substituted-hydrocarbyl radicals wherein one or more

1 hydrogen atoms is replaced by a halogen atom, hydrocarbyl-
2 substituted metalloids wherein the metalloid is selected
3 from Group IV-A of the Periodic Table of the Elements, halogen
4 radicals and the like. Suitable hydrocarbyl and substituted-
5 hydrocarbyl radicals which may be substituted for at least one
6 hydrogen atom in the cyclopentadienyl radical will contain from 1
7 to about 20 carbon atoms and include straight and branched alkyl
8 radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic
9 hydrocarbon radicals, aromatic radicals and alkyl-substituted
10 aromatic radicals. Similarly, and when X_1 and/or X_2 is a
11 hydrocarbyl or substituted-hydrocarbyl radical, each may,
12 independently, contain from 1 to about 20 carbon atoms and be a
13 straight or branched alkyl radical, a cyclic hydrocarbyl radical,
14 an alkyl-substituted cyclic hydrocarbyl radical, an aromatic
15 radical or an alkyl-substituted aromatic radical. Suitable
16 organo-metalloid radicals include mono-, di- and trisubstituted
17 organo-metalloid radicals of Group IV-A elements wherein each of
18 the hydrocarbyl Groups contains from 1 to about 20 carbon atoms.
19 Suitable organo-metalloid radicals include trimethylsilyl, tri-
20 ethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenyl-
21 germyl, trimethylgermyl and the like.

22 Illustrative, but not limiting examples of bis(cyclo-
23 pentadienyl)zirconium compounds which may be used in the
24 preparation of the improved catalyst of this invention are
25 dihydrocarbyl-substituted bis(cyclopentadienyl)zirconium compounds
26 such as bis(cyclopentadienyl)zirconium dimethyl,
27 bis(cyclopentadienyl)zirconium diethyl, bis(cyclopentadienyl)
28 zirconium dipropyl, bis(cyclopentadienyl)zirconium dibutyl,
29 bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)
30 zirconium dineopentyl, bis(cyclopentadienyl)zirconium di(m-tolyl),
31 bis(cyclopentadienyl)zirconium di(p-tolyl) and the like;
32 (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds
33 such as (methylcyclopentadienyl)(cyclopentadienyl) and
34 bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclo-
35 pentadienyl)(cyclopentadienyl) and bis(ethylcyclopentadienyl)
36 zirconium dimethyl, (propylcyclopentadienyl)(cyclopentadienyl) and
37 bis(propylcyclopentadienyl)zirconium dimethyl, (n-butylcyclo-

1 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)
2 zirconium dimethyl, (t-butylcyclopentadienyl)(cyclopentadienyl) and
3 bis(t-butylcyclopentadienyl)zirconium dimethyl, (cyclohexylmethyl-
4 cyclopentadienyl)(cyclopentadienyl) and bis(cyclohexylmethylcyclo-
5 pentadienyl)zirconium dimethyl, (benzylcyclopentadienyl)
6 (cyclopentadienyl) and bis(benzylcyclopentadienyl)zirconium
7 dimethyl, (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and
8 bis(diphenylmethylcyclopentadienyl)zirconium dimethyl,
9 (methylcyclopentadienyl)(cyclopentadienyl) and bis(methylcyclo-
10 pentadienyl)zirconium dihydride, (ethylcyclopenta dienyl)
11 (cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium
12 dihydride, (propylcyclopentadienyl)(cyclopentadienyl) and
13 bis(propylcyclopentadienyl)zirconium dihydride, (n-butylcyclo-
14 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)
15 zirconium dihydride, (t-butylcyclopentadienyl)(cyclopentadienyl)
16 and bis(t-butylcyclopentadienyl)zirconium dihydride,
17 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and
18 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,
19 (benzylcyclopentadienyl)(cyclopentadienyl) and bis(benzyl-
20 cyclopentadienyl)zirconium dihydride, (diphenylmethylcyclo-
21 pentadienyl)(cyclopentadienyl) and bis(diphenylmethylcyclopenta-
22 dienyl)zirconium dihydride and the like; (polyhydrocarbyl-
23 substituted-cyclopentadienyl)zirconium compounds such as
24 (dimethylcyclopentadienyl)(cyclopentadienyl) and bis(dimethylcyclo-
25 pentadienyl)zirconium dimethyl, (trimethylcyclopentadienyl)
26 (cyclopentadienyl) and bis(trimethylcyclopentadienyl)zirconium
27 dimethyl, (tetramethylcyclopentadienyl)(cyclopentadienyl) and
28 bis(tetramethylcyclopentadienyl)zirconium dimethyl,
29 (permethylcyclopentadienyl)(cyclopentadienyl) and bis(permethyl-
30 cyclopentadienyl)zirconium dimethyl, (ethyltetramethylcyclopenta-
31 dienyl)(cyclopentadienyl) and bis(ethyltetramethylcyclopentadienyl)
32 zirconium dimethyl, (indenyl)(cyclopentadienyl) and bis(indenyl)
33 zirconium dimethyl, (dimethylcyclopentadienyl)(cyclopentadienyl)
34 and bis(dimethylcyclopentadienyl)zirconium dihydride,
35 (trimethylcyclopentadienyl)(cyclopentadienyl) and bis(trimethyl-
36 cyclopentadienyl)zirconium dihydride, (tetramethylcyclopenta-
37 dienyl) (cyclopentadienyl) and bis(tetramethylcyclo-

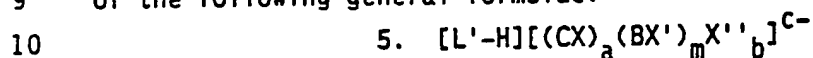
1 pentadienyl)zirconium dihydride, (permethylcyclopentadienyl)
2 (cyclopentadienyl) and bis(permethylcyclopentadienyl)zirconium
3 dihydride, (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and
4 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,
5 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride and
6 the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium
7 compounds such as (trimethylsilylcyclopentadienyl)(cyclopenta-
8 dienyl) and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,
9 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and bis(tri-
10 methylgermylcyclopentadienyl)zirconium dimethyl, (trimethyl-
11 stannylcyclopentadienyl)(cyclopentadienyl) and
12 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,
13 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
14 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,
15 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and
16 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,
17 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and
18 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,
19 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and
20 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,
21 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and
22 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the
23 like; (halogen-substituted-cyclopentadienyl)zirconium compounds
24 such as (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
25 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl,
26 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and
27 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the
28 like; silyl-substituted bis(cyclopentadienyl)zirconium compounds
29 such as bis(cyclopentadienyl)(trimethylsilyl)(methyl)zirconium,
30 bis(cyclopentadienyl)(triphenylsilyl)(methyl)zirconium,
31 bis(cyclopentadienyl)[tris(dimethylsilyl)silyl](methyl)zirconium,
32 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,
33 bis(cyclopentadienyl)(trimethylsilyl)(trimethylsilylmethyl)zirconium,
34 bis(cyclopentadienyl)(trimethylsilyl)(benzyl) and the like;
35 (bridged-cyclopentadienyl)zirconium compounds such as methylene
36 bis(cyclopentadienyl)zirconium dimethyl, ethylene
37 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl

1 bis(cyclopentadienyl)zirconium dimethyl, methylene bis(cyclopentad-
2 ienyl)zirconium dihydride, ethylene bis(cyclopentadienyl)zirconium
3 dihydride and dimethylsilyl bis(cyclopentadienyl)zirconium
4 dihydride and the like; zirconacycles such as bis(pentamethylcyclo-
5 pentadienyl) zirconacyclobutane, bis(pentamethylcyclopentadienyl)
6 zirconacyclopentane, bis(cyclopentadienyl)zirconaindane and the
7 like; olefin, diolefin and aryne ligand substituted bis(cyclop-
8 entadienyl)zirconium compounds such as bis(cyclopentadienyl)
9 (1,3-butadiene)zirconium, bis(cyclopentadienyl) (2,3-dimethyl-1,3-
10 butadiene)zirconium, bis(pentamethylcyclopentadienyl)(benzyne)
11 zirconium and the like; (hydrocarbyl)(hydride) bis(cyclopenta-
12 dienyl)zirconium compounds such as bis(pentamethylcyclopenta-
13 dienyl)zirconium (phenyl)(hydride), bis(pentamethylcyclopenta-
14 dienyl)zirconium (methyl)(hydride) and the like; and bis(cyclo-
15 pentadienyl)zirconium compounds in which a substituent on the
16 cyclopentadienyl radical is bound to the metal such as
17 (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylene)
18 zirconium hydride, (pentamethylcyclopentadienyl)(tetramethylcyclo-
19 pentadienylmethylene) zirconium phenyl and the like.

20 A similar list of illustrative bis(cyclopentadienyl)
21 hafnium and bis(cyclopentadienyl)titanium compounds could be made,
22 but since the lists would be nearly identical to that already
23 presented with respect to bis(cyclopentadienyl)zirconium compounds,
24 such lists are not deemed essential to a complete disclosure.
25 Those skilled in the art, however, are aware that bis(cyclo-
26 pentadienyl)hafnium compounds and bis(cyclopentadienyl) titanium
27 compounds corresponding to certain of the bis(cyclopentadienyl)
28 zirconium compounds listed supra are not known. The lists would,
29 therefore, be reduced by these compounds. Other bis(cyclopenta-
30 dienyl)hafnium compounds and other bis(cyclopentadienyl)titanium
31 compounds as well as other bis(cyclopentadienyl)zirconium compounds
32 which are useful in the catalyst compositions of this invention
33 will, of course, be apparent to those skilled in the art.

34 Compounds useful as a second component in the preparation
35 of the catalyst of this invention will comprise a cation, which is
36 a Bronsted acid capable of donating a proton, and a compatible

1 anion containing a plurality of boron atoms, which anion is
 2 relatively large, capable of stabilizing the active catalyst
 3 species which is formed when the two compounds are combined and
 4 said anion will be sufficiently labile to be displaced by olefinic,
 5 diolefinic and acetylenically unsaturated substrates or other
 6 neutral Lewis bases such as ethers, nitriles and the like. In
 7 general, a second compound useful in the preparation of the
 8 catalysts of this invention may be any compound represented by one
 9 of the following general formulae:



11 Wherein:

12 $L'-H$ is either H^+ , ammonium or a substituted ammonium
 13 cation having up to 3 hydrogen atoms replaced with a
 14 hydrocarbyl radical containing from 1 to about 20 carbon
 15 atoms or a substituted-hydrocarbyl radical, wherein one or
 16 more of the hydrogen atoms is replaced by a halogen atom,
 17 containing from 1 to about 20 carbon atoms, phosphonium
 18 radicals, substituted-phosphonium radicals having up to 3
 19 hydrogen atoms replaced with a hydrocarbyl radical
 20 containing from 1 to about 20 carbon atoms or a
 21 substituted-hydrocarbyl radical, wherein 1 or more of the
 22 hydrogen atoms is replaced by a halogen atom, containing
 23 from 1 to about 20 carbon atoms and the like; B and C are,
 24 respectively, boron and carbon; X, X' and X'' are radicals
 25 selected, independently, from the Group consisting of
 26 hydride radicals, halide radicals, hydrocarbyl radicals
 27 containing from 1 to about 20 carbon atoms,
 28 substituted-hydrocarbyl radicals, wherein one or more of
 29 the hydrogen atoms is replaced by a halogen atom,
 30 containing from 1 to about 20 carbon atoms, organo-
 31 metalloid radicals wherein each hydrocarbyl substitution
 32 in the organo portion contains from 1 to about 20 carbon
 33 atoms and said metal is selected from Group IV-A of the
 34 Periodic Table of the Elements and the like; a and b are
 35 integers ≥ 0 ; c is an integer ≥ 1 ; $a + b + c =$ an
 36 even-numbered integer from 2 to about 8; and m is an
 37 integer ranging from 5 to about 22.

1 6. $[L'-H][[(CX_3)_a, (BX_4)_m, (X_5)_b,]^{c'}]_2 M^{n+}]^d-$

2 Wherein:

3 $L'-H$ is either H^+ , ammonium or a substituted ammonium
 4 radical having up to 3 hydrogen atoms replaced with a
 5 hydrocarbyl radical containing from 1 to about 20 carbon
 6 atoms or a substituted-hydrocarbyl radical, wherein 1 or
 7 more of the hydrogen atoms is replaced by a halogen atom,
 8 containing from 1 to about 20 carbon atoms, a phosphonium
 9 radical, a substituted-phosphonium radical having up to 3
 10 hydrogen atoms replaced with a hydrocarbyl radical
 11 containing from 1 to about 20 carbon atoms or a
 12 substituted-hydrocarbyl radical, wherein 1 or more of the
 13 hydrogen atoms is replaced by a halogen atom, containing
 14 from 1 to about 20 carbon atoms and the like; B, C, M and
 14 H are, respectively, boron; carbon, a transition metal and
 15 hydrogen; X_3 , X_4 , and X_5 are radicals selected,
 16 independently, from the Group consisting of hydride
 17 radicals, halide radicals, hydrocarbyl radicals containing
 18 from 1 to about 20 carbon atoms, substituted-hydrocarbyl
 19 radicals, wherein one or more of the hydrogen atoms is
 20 replaced by a halogen atom, containing from 1 to about 20
 21 carbon atoms, organo-metalloid radicals wherein each
 22 hydrocarbyl substitution in the organo portion or said
 23 organo-metalloid contains from 1 to about 20 carbon atoms
 24 and said metal is selected from Group IV-A of the Periodic
 25 Table of the Elements and the like; a' and b' are the same
 26 or a different integer ≥ 0 ; c' is an integer ≥ 2 ;
 27 $a' + b' + c' =$ an even-numbered integer from 4 to about 8;
 28 m' is an integer from 6 to about 12; n is an integer such
 29 that $2c' - n = d$; and d is an integer ≥ 1 .

30 Illustrative, but not limiting, examples of the second
 31 compounds which can be used as a second component in the catalyst
 32 compositions of this invention are ammonium salts such as ammonium
 33 1-carbadodecaborate (using 1-carbadodecaborate as an illustrative,
 34 but not limiting, counterion for the ammonium cations listed
 35 below): monohydrocarbyl-substituted ammonium salts such as
 36 methylammonium 1-carbadodecaborate, ethylammonium 1-carbadode-

1 caborate, propylammonium 1-carbadodecaborate, isopropylammonium
2 1-carbadodecaborate, (n-butyl)ammonium 1-carbadodecaborate,
3 anilinium 1-carbadodecaborate, and (p-tolyl)ammonium
4 1-carbadodecaborate and the like; dihydrocarbyl-substituted
5 ammonium salts such as dimethylammonium 1-carbadodecaborate,
6 diethylammonium 1-carbadodecaborate, dipropylammonium
7 1-carbadodecaborate, diisopropylammonium 1-carbadodecaborate,
8 di(n-butyl)ammonium 1-carbadodecaborate, diphenylammonium
9 1-carbadodecaborate, di(p-tolyl)ammonium 1-carbadodecaborate and
10 the like; trihydrocarbyl-substituted ammonium salts such as
11 trimethylammonium 1-carbadodecaborate, triethylammonium
12 1-carbadodecaborate, tripropylammonium 1-carbadodecaborate,
13 tri(n-butyl) ammonium 1-carbadodecaborate, triphenylammonium
14 1-carbadodecaborate, tri(p-tolyl)ammonium 1-carbadodecaborate,
15 N,N-dimethylanilinium 1-carbadodecaborate, N,N-diethylanilinium
16 1-carbadodecaborate and the like.

17 Illustrative, but not limiting examples of second
18 compounds corresponding to Formula 5 [using tri(n-butyl)ammonium as
19 an illustrative, but not limiting, counterion for the anions listed
20 below] are salts of anions such as bis[tri(n-butyl)ammonium]
21 nonaborate, bis[tri(n-butyl)ammonium]decaborate,
22 bis[tri(n-butyl)ammonium]undecaborate, bis[tri(n-butyl)ammonium]
23 dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate,
24 bis[tri(n-butyl)ammonium]dodecachlorododecaborate,
25 tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium
26 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate,
27 tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate,
28 tri(n-butyl)ammonium dibromo-1-carbadodecaborate and the like;
29 borane and carborane complexes and salts of borane and carborane
30 anions such as decaborane(14), 7,8-dicarbaundecaborane(13),
31 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-
32 dicarbaundecaborane, dodecahydrido-11-methyl-2,7-di-
33 carbaundecaborane, tri(n-butyl)ammonium undecaborate(14),
34 tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium
35 7-carbaundecaborate(13), tri(n-butyl)ammonium 7,8-dicarbaunde-
36 caborate(12), tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),
37 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaunde-

1 caborate, tri(n-butyl)ammonium undecahydrido-8-ethyl-
2 7,9-dicarbaundecaborate, tri(n-butyl)ammonium undecahydrido-
3 8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium
4 undecahydrido-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium
5 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,
6 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate
7 and the like; boranes and carboranes and salts of boranes and
8 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanona-
9 borane(13), 6,9-dicarbadeceborane(14), dodecahydrido-1-
10 phenyl-1,3-dicarbanonaborane, dodecahydrido-1-methyl-1,3-
11 dicarbanonaborane, undecahydrido-1,3-dimethyl-1,3-dicarbanona-
12 borane and the like.

13 Illustrative, but not limiting, examples of second
14 compounds corresponding to Formula 6 [using tri(n-butyl)ammonium as
15 an illustrative, but not limiting, counterion for the anions listed
16 below] are salts of metallacarborane and metallaborane anions such
17 as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)
18 cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-
19 dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undeca-
20 hydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)
21 ammonium bis(undecahydrido-7,8-dicarbaundecaborato)nickelate(III),
22 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)
23 cuprate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicar-
24 baundecaborato)aurate(III), tri(n-butyl)ammonium bis(nonahydrido-
25 7,8-dimethyl-7,8-dicarbaundecaborato)-ferrate(III), tri(n-butyl)
26 ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)
27 chromate(III), tri(n-butyl)ammonium bis(tribromooctahydrido-
28 7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium
29 bis(dodecahydridodicarbadeceborato)cobaltate(III),
30 bis[tri(n-butyl)ammonium] bis(dodecahydridodeceborato)
31 nickelate(II), tris[tri(n-butyl)ammonium] bis(undecahydrido-7-
32 carbaundecaborato)chromate(III), bis[tri(n-butyl) ammonium]
33 bis(undecahydrido-7-carbaundecaborato)manganate(IV),
34 bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)
35 cobaltate(III), bis[tri(n-butyl)ammonium] bis(undecahydrido-7-
36 carbaundecaborato)nickelate(IV) and the like. A similar list of
37 representative phosphonium compounds could be recited as

1 illustrative second compounds, but for the sake of brevity, it is
2 simply noted that the phosphonium and substituted-phosphonium salts
3 corresponding to the listed ammonium and substituted-ammonium salts
4 could be used as second compounds in the present invention.

5 In general, and while most first components identified
6 above may be combined with most second components identified above
7 to produce an active olefin polymerization catalyst, it is
8 important to continued polymerization operations that either the
9 initially formed metal cation or a decomposition product thereof be
10 a relatively stable olefin polymerization catalyst. It is also
11 important that the anion of the second compound be stable to
12 hydrolysis when an ammonium salt is used. Further, it is important
13 that the acidity of the second component be sufficient, relative to
14 the first, to facilitate the needed proton transfer. Conversely,
15 the basicity of the metal complex must also be sufficient to
16 facilitate the needed proton transfer. Certain metallocene
17 compounds—using bis(pentamethylcyclopentadienyl)hafnium dimethyl
18 as an illustrative, but not limiting example—are resistant to
19 reaction with all but the strongest Bronsted acids and thus are not
20 suitable as first components to form the catalysts described
21 herein. In general, bis(cyclopentadienyl)metal compounds which can
22 be hydrolyzed by aqueous solutions can be considered suitable as
23 first components to form the catalysts described herein.

24 With respect to the combination of the desired cation and
25 the stabilizing anion to form an active catalyst of the present
26 invention, it should be noted that the two compounds combined for
27 preparation of the active catalyst must be selected so as to ensure
28 displacement of the anion by monomer or another neutral Lewis
29 base. This could be done by steric hindrance, resulting from
30 substitutions on the cyclopentadienyl carbon atoms as well as from
31 substitutions on the anion itself. The use of perhydrocarbyl-
32 substituted cyclopentadienyl metal compounds and/or bulky second
33 components does not generally prevent the desired combination and,
34 in fact, generally yields more labile anions. It follows, then,
35 that metal compounds (first components) comprising perhydrocarbyl-
36 substituted cyclopentadienyl radicals could be effectively used
37 with a wider range of second compounds than could metal compounds

1 (first components) comprising unsubstituted cyclopentadienyl
2 radicals. In fact, first compounds comprising perhydrocarbyl-
3 substituted cyclopentadienyl radicals would, generally, be
4 effective when used in combination with second components having
5 both larger and smaller anions. As the amount and size of the
6 substitutions on the cyclopentadienyl radicals are reduced,
7 however, more effective catalysts are obtained with second
8 compounds containing larger anions, such as those encompassed by
9 Equation 6 above and those having larger m values in Equation 5.
10 In these cases, it is further preferable that in using second
11 compounds which are encompassed by Equation 5, $a + b + c = 2$.
12 Second compounds in which $a + b + c =$ even-numbered integers of 4
13 or more have acidic B-H-B moieties which can react further with the
14 metal cation formed, leading to catalytically inactive compounds.

15 In general, the catalyst can be prepared by combining the
16 two components in a suitable solvent at a temperature within the
17 range from about -100°C to about 300°C . The catalyst may be used
18 to polymerize α -olefins and acetylenically unsaturated monomers
19 having from two to about eighteen carbon atoms and diolefins having
20 from four to about eighteen carbon atoms either alone or in
21 combination. The catalyst may also be used to polymerize
22 α -olefins, diolefins and/or acetylenically unsaturated monomers
23 in combination with other unsaturated monomers. In general, the
24 polymerization will be accomplished at conditions well known in the
25 prior art for the polymerization of monomers of this type. It
26 will, of course, be appreciated that the catalyst system will form
27 in situ if the components thereof are added directly to the
28 polymerization process and a suitable solvent or diluent is used in
29 said polymerization process. It is, however, preferred, to form
30 the catalyst in a separate step prior to adding the same to the
31 polymerization step. While the catalysts do not contain pyrophoric
32 species, the catalyst components are sensitive to both moisture and
33 oxygen and should be handled and transferred in an inert atmosphere
34 such as nitrogen, argon or helium.

35 As indicated supra, the improved catalyst of the present
36 invention will, generally, be prepared in a suitable solvent or
37 diluent. Suitable solvents or diluents include any of the solvents

1 known in the prior art to be useful as solvents in the
2 polymerization of olefins. Suitable solvents, then, include, but
3 are not necessarily limited to, straight and branched-chain
4 hydrocarbons such as isobutane, butane, pentane, hexane, heptane,
5 octane and the like, cyclic and alicyclic hydrocarbons such as
6 cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane
7 and the like and aromatic and alkyl substituted aromatic compounds
8 such as benzene, toluene, xylene and the like. Suitable solvents
9 also include basic solvents not heretofore useful as polymerization
10 solvents when conventional Ziegler-Natta type polymerization
11 catalysts are used such as chlorobenzene, dichloromethane and
12 propyl chloride.

13 While the inventors do not wish to be bound by any
14 particular theory, it is believed that when the two compounds used
15 to prepare the improved catalysts of the present invention are
16 combined in a suitable solvent or diluent, all or a part of the
17 cation of the second compound (the proton) combines with one of the
18 substituents on the metal-containing (first) component. In the
19 case where the first component has a formula corresponding to that
20 of general formula 1 supra, a neutral compound is liberated which
21 either remains in solution or is liberated as a gas. In this
22 regard, it should be noted that if the cation of the second
23 compound is a proton and either X_1 or X_2 in the metal
24 containing (first) compound is a hydride, hydrogen gas may be
25 liberated. Similarly, if the cation of the second compound is a
26 proton and either X_1 or X_2 is a methyl radical, methane may be
27 liberated as a gas. In the cases where the first component has a
28 formula corresponding to those of general formulae 2, 3 or 4, one
29 of the substituents on the metal-containing (first) component is
30 protonated but, in general, no substituent is liberated from the
31 metal. It is preferred that the ratio of metal containing (first)
32 component to second component cations be about 1:1 or greater. The
33 conjugate base of the cation of the second compound, if such a
34 portion does remain, will be a neutral compound which will remain
35 in solution or complex with the metal cation formed, though, in
36 general, a cation is chosen such that any binding of the neutral
37 conjugate base to the metal cation will be weak or nonexistent.

1 Thus, as the steric bulk of this conjugated base increases, it
2 will, simply, remain in solution without interfering with the
3 active catalyst. For example, if the cation of the second compound
4 is an ammonium ion, this ion will liberate a hydrogen atom which
5 may then react as in the case when the hydrogen atom was the cation
6 to form gaseous hydrogen, methane or the like and the conjugate
7 base of the cation will be ammonia. In like fashion, if the cation
8 of the second compound were a hydrocarbyl-substituted ammonium ion
9 containing at least one hydrogen atom, as is essential to the
10 present invention, the hydrogen atom would be given up to react in
11 the same fashion as when hydrogen were the cation and the conjugate
12 base of the cation would be an amine. Further, if the cation of
13 the second compound were a hydrocarbyl-substituted phosphonium ion
14 containing at least one proton, as is essential to the present
15 invention, the conjugate base of the cation would be phosphine.

16 While still not wishing to be bound by any particular
17 theory, it is also believed that when the metal containing (first)
18 component has reacted with the second component, the non-
19 coordinating anion originally contained in the second compound used
20 in the catalyst preparation combines with and stabilizes either the
21 metal cation, formally having a coordination number of 3 and a +4
22 valence, or a decomposition product thereof. The cation and anion
23 will remain so combined until the catalyst is contacted with one or
24 more olefins, diolefins and/or acetylenically unsaturated monomers
25 either alone or in combination with one or more other monomers. As
26 indicated supra, the anion contained in the second compound must be
27 sufficiently labile to permit rapid displacement by an olefin, a
28 diolefin or an acetylenically unsaturated monomer to facilitate
29 polymerization.

30 As indicated supra, most first compounds identified above
31 will combine with most second compounds identified above to produce
32 an active catalyst, particularly an active polymerization
33 catalyst. The actual active catalyst species is not, however,
34 always sufficiently stable as to permit its separation and
35 subsequent identification. Moreover, and while many of the
36 initial metal cations are relatively stable, it has become apparent
37 that the initially formed metal cation may decompose yielding

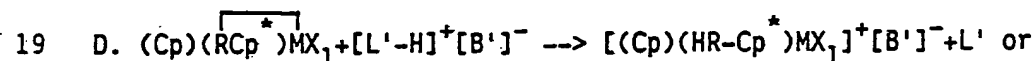
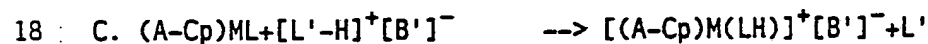
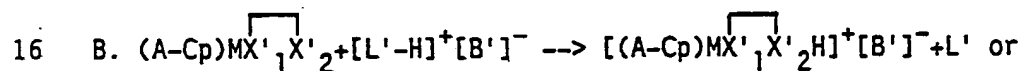
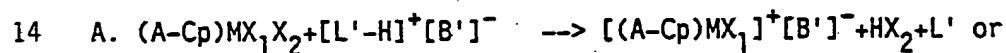
1 either an active polymerization catalyst species or a catalytically
2 inactive species. Most decomposition products are, however,
3 catalytically active. While the inventors still do not wish to be
4 bound by any particular theory, it is believed that the active
5 catalyst species which have not been isolated, including active
6 decomposition products, are of the same type as those which have
7 been isolated and fully characterized or at least retain the
8 essential structure required for functioning as a catalyst such as
9 a reactive metal-carbon bond.

10 While still not wishing to be bound by any particular
11 theory and as indicated supra, it is also believed that the extent
12 and nature of the substitution on the cyclopentadienyl ring
13 dictates the size of the stabilizing anion needed to generate a
14 particularly active olefin polymerization catalyst. In this
15 regard, it is believed that as the number of substituents on the
16 cyclopentadienyl radical in the metallocene cation are decreased
17 from 5 to 0, a given anion will become increasingly less labile.
18 Thus, it is suggested that as the number of substituents on the
19 cyclopentadienyl radical in the metallocene cation are reduced from
20 5 to 0, larger or less reactive anions should be used to ensure
21 lability and allow for the generation of a particularly active
22 catalyst species.

23 Consistent with the foregoing, stable, isolable,
24 characterizable olefin polymerization catalysts have been prepared
25 when bis(permethylocyclopentadienyl)zirconium dimethyl has been
26 combined with and reacted with tri(n-butyl)ammonium
27 7,8-dicarbaundecaborate(12) or 7,8-dicarbaundecaborane(13). A
28 stable, isolable, olefin polymerization catalyst has also been
29 prepared when bis(ethyltetramethylcyclopentadienyl)zirconium
30 dimethyl has been combined with 7,8-dicarbaundecaborane(13). In
31 each of these cases, the stable polymerization catalyst was
32 prepared by adding the reactants into a suitable solvent or diluent
33 at a temperature within the range from about -100°C to about
34 300°C. Based on this and other information available to the
35 inventors, it appears clear that isolable and characterizable
36 polymerization catalysts can also be prepared when a
37 bis(perhydrocarbyl-substituted cyclopentadienyl)metal compound is

1 combined with any one or more of the second compounds identified
 2 above. Also, active, but unisolated polymerization catalysts are
 3 prepared when bis(cyclopentadienyl)zirconium compounds containing
 4 less than five hydrocarbyl-substitutions on each cyclopentadienyl
 5 radical are reacted with a suitable second compound, within the
 6 scope of the present invention, containing a cation capable of
 7 donating a proton and an anion capable of stabilizing the
 8 metallocene cation and sufficiently labile to be displaced by an
 9 olefin, a diolefin or an acetylenically unsaturated monomer during
 10 polymerization, particularly those second compounds having the
 11 larger anions.

12 The chemical reactions which occur may be represented by
 13 reference to the general formulae set forth herein as follows:



21 In the foregoing reaction equations, the letters A-D
 22 correspond to the numbers 1-4, respectively, set forth in
 23 combination with the general equations for useful metallocene
 24 compounds. B' represents a compatible ion corresponding to the
 25 general formulae outlined in formulae 5 and 6 above. The reaction

1 of each of the four classes of metallocenes with N,N-dimethyl-
2 anilinium bis(7,8-dicarbaundecaborato)cobaltate(III) has been
3 examined by solution ^1H NMR or ^{13}C NMR spectroscopy. In each
4 case, products conforming to those outlined above were observed.

5 In general, the stable, isolable catalysts formed by the
6 method of this invention may be separated from the solvent and
7 stored for subsequent use. The unisolated catalysts, however,
8 will, generally, be retained in solution until ultimately used in
9 the polymerization of olefins. Alternatively, any of the catalysts
10 prepared by the method of this invention may be retained in
11 solution for subsequent use or used directly after preparation as a
12 polymerization catalyst. Moreover, and as indicated supra, the
13 catalysts may be prepared in situ by passing the separate
14 components into the polymerization vessel where the components will
15 be contacted and react to produce the improved catalyst of this
16 invention.

17 In general, and as indicated supra, the improved catalyst
18 of this invention will polymerize olefins, diolefins and/or
19 acetylenically unsaturated monomers either alone or in combination
20 with other olefins and/or other unsaturated monomers at conditions
21 well known in the prior art for conventional Ziegler-Natta
22 catalysis. In the polymerization process of this invention, the
23 molecular weight appears to be a function of both catalyst
24 concentration, polymerization temperature and polymerization
25 pressure. In general, the polymers produced with the catalyst of
26 this invention, when produced in an atmosphere free of hydrogen or
27 other chain terminating agents, will contain terminal unsaturation.

28 The polymer products produced with the catalyst of this
29 invention will, of course, be free of certain trace metals
30 generally found in polymers produced with Ziegler-Natta type
31 catalysts such as aluminum, magnesium, chloride and the like. The
32 polymer products produced with the catalysts of this invention
33 should then have a broader range of applications than polymers
34 produced with more conventional Ziegler-Natta type catalysts
35 comprising a metal alkyl, such as an aluminum alkyl.

1 PREFERRED EMBODIMENT OF THE INVENTION

2 In a preferred embodiment of the present invention, a
 3 polymerization catalyst will be prepared by combining a
 4 bis(cyclopentadienyl) compound of one of the Group IV-B metals,
 5 most preferably a bis(cyclopentadienyl)zirconium or
 6 bis(cyclopentadienyl)hafnium compound, containing two independently
 7 substituted or unsubstituted cyclopentadienyl radicals and two
 8 lower alkyl substituents or two hydrides with one of the following:

9 (1). A trisubstituted ammonium salt of a borane or
 10 carborane anion satisfying the general formula:



12 Wherein:

13 B, C, and H are, respectively, boron, carbon and hydrogen;
 14 ax is either 0 or 1; cx is either 1 or 2; ax + cx = 2; and
 15 bx is an integer ranging from 10 to 12.

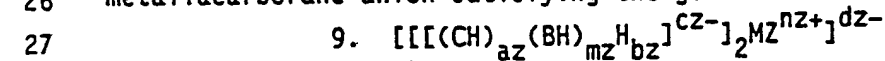
16 (2). A trisubstituted ammonium salt of a borane or
 17 carborane anion or a neutral borane or carborane compound
 18 satisfying the general formula:



20 Wherein:

21 B, C and H are, respectively, boron, carbon and hydrogen;
 22 ay is an integer from 0 to 2; by is an integer from 0 to 3;
 23 cy is an integer from 0 to 3; ay + by + cy = 4; and my is
 24 an integer from 9 to 18.

25 (3). A trisubstituted ammonium salt of a metallaborane or
 26 metallacarborane anion satisfying the general formula:



28 Wherein:

29 B, C, H and MZ are, respectively, boron, carbon, hydrogen
 30 and a transition metal; az is an integer from 0 to 2; bz
 31 is an integer from 0 to 2; cz is either 2 or 3;
 32 mz is an integer from 9 to 11; az + bz + cz = 4; and nz
 33 and dz are, respectively, 2 & 2 or 3 & 1.

34 Each of the trisubstitutions in the ammonium cation will
 35 be the same or a different lower alkyl or aryl radical. By lower
 36 alkyl is meant an alkyl radical containing from one to four carbon

1 atoms. In a most preferred embodiment of the present invention
2 wherein an anion represented by Formula 7 is used,
3 bis(pentamethylcyclopentadienyl)zirconium dimethyl will be combined
4 with tri(n-butyl)ammonium 1-carbaundecaborate to produce a most
5 preferred catalyst. In a most preferred embodiment of the present
6 invention wherein an anion represented by Formula 8 is used,
7 bis(pentamethylcyclopentadienyl)zirconium dimethyl will be combined
8 with 7,8-dicarbaundecaborane(13) to produce a most preferred
9 catalyst. In a most preferred embodiment of the present invention
10 wherein an anion represented by Formula 9 is used,
11 bis(cyclopentadienyl)zirconium or -hafnium dimethyl will be
12 combined with N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
13 cobaltate(III) to produce a most preferred catalyst. In a
14 preferred embodiment of this invention, the two components used to
15 prepare the catalyst will be combined at a temperature within the
16 range from about 0°C to about 100°C. The components will be
17 combined, preferably, in an aromatic hydrocarbon solvent, most
18 preferably toluene. Nominal holding times within the range from
19 about 10 seconds to about 60 minutes will be sufficient to produce
20 both the preferred and most preferred catalysts of this invention.

21 In a preferred and most preferred embodiment of this
22 invention, the catalyst, immediately after formation, will be used
23 to polymerize one or more lower α -olefins, particularly ethylene
24 and propylene, most preferably ethylene, at a temperature within
25 the range from about 0°C to about 100°C and at a pressure within
26 the range from about 15 to about 500 psig. The monomers will be
27 maintained at polymerization conditions for a nominal holding time
28 within the range from about 1 to about 60 minutes and the catalyst
29 will be used at a concentration within the range of about 10^{-5} to
30 about 10^{-1} moles per liter of solvent or diluent.

31 Having thus broadly described the present invention and a
32 preferred and most preferred embodiment thereof, it is believed
33 that the same will become even more apparent by reference to the
34 following examples. It will be appreciated, however, that the
35 examples are presented solely for purposes of illustration and
36 should not be construed as limiting the invention. In the examples
37 wherein an active catalyst was isolated and identified, the

1 analysis was by solid-state ^{13}C NMR spectroscopy and solution
2 ^1H NMR spectroscopy.

3 EXAMPLE 1

4 In this example, an active olefin polymerization catalyst
5 was prepared and isolated by combining 1.0 g of bis(pentamethyl-
6 cyclopentadienyl)zirconium dimethyl in 50 ml toluene and then
7 adding 0.82 g of tri(n-butyl)ammonium 7,8-dicarbaundecaborate(12).
8 The mixture was stirred at room temperature for 30 minutes, the
9 solvent was evaporated to half its original volume and pentane
10 added to the point of cloudiness. After cooling at -20°C
11 overnight, a yellow solid was filtered off, washed with pentane and
12 dried. The yield of active catalyst was 0.75 g. A portion of this
13 product was analyzed and identified as bis(pentamethylcyclopenta-
14 dienyl)methyl(dodecahydrido-7,8-dicarbaundecaborato)zirconium.

15 EXAMPLE 2

16 In this example, an active olefin polymerization catalyst
17 was prepared by dissolving 1.2 g of bis(pentamethylcyclopenta-
18 dienyl)zirconium dimethyl in 100 ml pentane and then adding
19 dropwise 5 ml of a toluene solution containing 0.38 g of
20 7,8-dicarbaundecaborane(13). A bright yellow solid precipitated
21 from solution. After thirty minutes, the solid was filtered off,
22 washed with pentane and dried. The yield of product was 0.95 g. A
23 portion of the product was analyzed and identified as bis(penta-
24 methylcyclopentadienyl)methyl(dodecahydrido-7,8-dicarbaundecaborato)
25 zirconium, the same active catalyst produced in Example 1.

26 EXAMPLE 3

27 In this example, an active olefin polymerization catalyst
28 was prepared by dissolving 0.425 g of bis(ethyltetramethylcyclo-
29 pentadienyl)zirconium dimethyl in 60 ml of pentane and adding
30 dropwise 5 ml of a toluene solution containing 0.125 g of
31 7,8-dicarbaundecaborane(13). A bright yellow solid precipitated
32 from solution. After fifteen minutes, the solid was filtered off,
33 washed with pentane and dried. The yield of product was 0.502 g.
34 A portion of the product was analyzed and identified as
35 bis(ethyltetramethylcyclopentadienyl)methyl(dodecahydrido-7,8-di-
36 carbaundecaborato)zirconium.

1 EXAMPLE 4

2 In this example, ethylene was polymerized using a portion
3 of the catalyst produced in Example 2 by dissolving 50 mg of the
4 catalyst in 100 ml of toluene and transferring the catalyst
5 solution under a nitrogen atmosphere into a stirred, steel 1 liter
6 autoclave which was previously flushed with nitrogen. The
7 autoclave was pressured with 300 psig ethylene and stirred at
8 60°C. After thirty minutes, the reactor was vented and opened.
9 The yield of linear polyethylene formed was 22.95 g.

10 EXAMPLE 5

11 In this example, ethylene was polymerized with the
12 catalyst produced in Example 3 by dissolving 50 mg of the catalyst
13 in 100 ml of toluene and transferring the catalyst solution under a
14 nitrogen atmosphere into a stirred, steel 1 liter autoclave which
15 was previously flushed with nitrogen. The autoclave was pressured
16 with 400 psig ethylene and stirred at 40°C. After one hour, the
17 reactor was vented and opened. The yield of linear polyethylene
18 formed was 74.6 g.

19 EXAMPLE 6

20 In this example, ethylene was again polymerized with a
21 portion of the catalyst produced in Example 2 by dissolving 75 mg
22 of the catalyst in 100 ml of chlorobenzene and transferring under a
23 nitrogen atmosphere into a stirred, steel 1 liter autoclave which
24 was previously flushed with nitrogen. The autoclave was pressured
25 with 150 psig ethylene and stirred at 40°C. After twenty minutes,
26 the reactor was vented and opened. The yield of linear poly-
27 ethylene formed was 3.3 g.

28 EXAMPLE 7

29 In this example, ethylene was polymerized with an active
30 catalyst formed in situ by dissolving 80 mg of bis(pentamethyl-
31 cyclopentadienyl)zirconium dimethyl and 35 mg of 1,2-dicarbaun-
32 decaborane(13) in 20 ml of dichloromethane. Ethylene was then
33 bubbled through the solution at atmospheric conditions for one
34 minute and the slurry then poured into an excess of ethanol. The
35 polyethylene formed was filtered off, washed with water and acetone
36 and dried. The yield of polyethylene was 1.6 g.

1 EXAMPLE 8

2 In this example, an active catalyst was prepared by
3 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (46 mg)
4 with octadecaborane(22) (20 mg) in toluene (5 ml). There was
5 considerable gas evolution. On passing ethylene through the
6 solution for one minute, the solution grew hot. The vial was
7 opened and acetone added to precipitate the polymer, which was
8 filtered off, washed with acetone, and dried. The yield of polymer
9 isolated was 0.32 g.

10 EXAMPLE 9

11 In this example, an active catalyst was prepared by
12 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)
13 with tri(n-butyl)ammonium tridecahydrido-7-carbaundecaborate (30
14 mg) in toluene (50 ml) in a serum-capped round-bottomed flask. The
15 solution turned from colorless to orange-yellow. On passing
16 ethylene through the solution for 1 minute, the solution grew hot
17 as polymer precipitated from solution.

18 EXAMPLE 10

19 In this example, an active catalyst was prepared in an NMR
20 tube by combining 50 mg of bis(pentamethylcyclopentadienyl)
21 zirconium dimethyl and 40 mg of tri(n-butyl)ammonium 1-carbado-
22 decaborate in 1 ml of hexadeuteriobenzene and placing the solution
23 into the NMR tube. The disappearance of starting material was then
24 observed by ^1H NMR spectroscopy and when the starting materials
25 had disappeared ethylene was injected into the NMR tube. Solid
26 polymer precipitated from the solution.

27 EXAMPLE 11

28 In this example, an active catalyst was again prepared in
29 an NMR tube by dissolving 100 mg of bis[1,3-bis(trimethylsilyl)
30 cyclopentadienyl]zirconium dimethyl and 60 mg of tri(n-butyl)
31 ammonium 1-carbadodecaborate in 1 ml of hexadeuteriobenzene and
32 then placing the solution into the NMR tube. The disappearance of
33 starting materials was observed in the ^1H NMR spectrum. When all
34 of the starting zirconium compound had disappeared, ethylene was
35 injected into the tube and solid polymer precipitated from solution.

1 EXAMPLE 12

2 In this example, an active catalyst was again formed in an
3 NMR tube by dissolving 100 mg of (pentamethylcyclopentadienyl)
4 [1,3-bis(trimethylsilyl)cyclopentadienyl]zirconium dimethyl and 70
5 mg of tri(n-butyl)ammonium 1-carbadodecaborate in 1 ml of
6 hexadeuteriobenzene and then placing the solution in the NMR tube.
7 Disappearance of starting material was followed by ^1H NMR
8 spectrum and when all of the starting zirconium compound had
9 disappeared ethylene was injected into the tube. Solid ethylene
10 polymer then precipitated from solution.

11 EXAMPLE 13

12 In this example, an active catalyst was prepared by
13 suspending 80 mg bis(pentamethylcyclopentadienyl)zirconium dimethyl
14 and 50 mg of bis[tri(n-butyl)ammonium]dodecaborate in 7 ml of
15 toluene in a serum capped vial. On mixing, the suspension turned
16 from colorless to yellow-green. Bubbling ethylene through the
17 solution for 30 seconds caused a white polymer to form as the
18 solution became warm. The vial was opened and the polymer
19 precipitated with ethanol. The yield of polyethylene was 0.13 g.

20 EXAMPLE 14

21 In this example, an active catalyst was prepared by
22 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (45 mg)
23 with tri(n-butyl)ammonium undecahydrido-1-carbaundecaborate (30 mg)
24 in toluene (5 ml) in a serum-capped vial. The solution turned from
25 colorless to yellow. On passing ethylene through the solution for
26 30 seconds, the solution grew hot as polymer precipitated.

27 EXAMPLE 15

28 In this example, an active catalyst was prepared by
29 suspending 80 mg of bis(pentamethylcyclopentadienyl)zirconium
30 dimethyl and 90 mg of N,N-dimethylanilinium bis(7,8-dicarbaun-
31 decaborato)cobaltate(III) in 5 ml of toluene in a serum-capped
32 vial. The yellow solution turned orange-violet with gas
33 evolution. On passing ethylene through the solution for 30
34 seconds, the solution turned deep violet with considerable
35 evolution of heat and became viscous. The vial was opened and the
36 solids precipitated with ethanol. These were washed with 10%

1 aqueous sodium hydroxide solution, ethanol, acetone and hexane.

2 The yield of polyethylene was 0.41 g.

3 EXAMPLE 16

4 In this example, an active catalyst was prepared by
5 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)
6 with N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)ferrate(III)
7 (45 mg) in toluene (10 ml) in a serum-capped vial. On passing
8 ethylene through the solution, the mixture grew hot as polymer
9 formed. The vial was opened and the contents diluted with acetone,
10 then filtered and dried. The yield of polymer isolated was 0.33 g.

11 EXAMPLE 17

12 In this example, an active catalyst was prepared by
13 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)
14 with tri(n-butyl)ammonium bis(7,8-dicarbaundecaborato)nickelate
15 (III) (45 mg) in toluene (30 ml) in a serum-capped round-bottomed
16 flask. Ethylene was passed through the solution for one minute.
17 The solution grew hot as polymer precipitated from solution. The
18 flask was opened and the contents diluted with acetone. The solid
19 polymer was filtered off, washed with acetone, and dried. The
20 yield of isolated polymer was 0.48 g.

21 EXAMPLE 18

22 In this example, an active catalyst was prepared by
23 suspending 100 mg of bis(methylcyclopentadienyl)zirconium dihydride
24 and 180 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
25 cobaltate(III) in 100 ml of toluene in a 250 ml round bottomed
26 flask capped with a rubber septum. Ethylene was bubbled through
27 the solution for 10 minutes. The flask was opened, the contents
28 poured into hexane, filtered off and dried. The yield of polymer
29 was 2.98 g.

30 EXAMPLE 19

31 In this example, an active catalyst was prepared by
32 suspending 105 mg of bis[1,3-bis(trimethylsilyl)cyclopenta-
33 dienyl]zirconium dimethyl and 90 mg of N,N-dimethylanilinium
34 bis(7,8-dicarbaundecaborato)cobaltate(III) in 50 ml of toluene in a
35 100 ml round bottomed flask capped with a rubber septum. Ethylene
36 was bubbled through the solution for 10 minutes. The flask was

1 opened and the contents poured into ethanol and evaporated. The
2 yield of polymer was 2.7 g.

3 EXAMPLE 20

4 In this example, an active catalyst was prepared by
5 stirring 50 mg of bis(cyclopentadienyl)zirconium dimethyl and 90 mg
6 of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III)
7 in 50 ml of toluene in a 100 ml round bottomed flask capped with a
8 rubber septum. On passing ethylene through the solution, no
9 obvious reaction was observed for one minute, after which a
10 pronounced turbidity could be seen. After 10 minutes, the flask
11 was opened, the contents diluted with ethanol and evaporated. The
12 yield of polymer was 1.9 g.

13 EXAMPLE 21

14 In this example, ethylene was polymerized by reacting 69
15 mg of bis(cyclopentadienyl)hafnium dimethyl with 90 mg of
16 N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III) in
17 50 ml of toluene in a septum-capped round bottomed flask. On
18 passing ethylene through the solution, a pronounced turbidity
19 appeared after 30 seconds as the solution grew hot. After 10
20 minutes, the solution was poured into acetone and the polymer
21 filtered off and dried. The yield of linear polyethylene was 2.2 g.

22 EXAMPLE 22

23 In this example, ethylene was polymerized by reacting 50
24 mg of bis(trimethylsilylcyclopentadienyl)hafnium dimethyl with 45
25 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
26 cobaltate(III) in 5 ml of toluene in a serum-capped vial. On
27 passing ethylene through the solution, polymer formed as the
28 mixture grew hot. After 1 minute, the vial was opened and the
29 contents diluted with acetone and filtered off. The yield of
30 linear polyethylene was 0.35 g.

31 EXAMPLE 23

32 In this example, ethylene and 1-butene were copolymerized
33 in a toluene diluent by adding under a nitrogen atmosphere to a 1
34 liter stainless-steel autoclave, previously flushed with nitrogen
35 and containing 400 ml of dry, oxygen-free toluene, 35 ml of a
36 toluene solution containing a catalyst prepared in situ from 50 mg
37 of bis(cyclopentadienyl)zirconium dimethyl and 45 mg of

1 N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III).
2 1-Butene (200 ml) was added to the autoclave, which was further
3 pressurized with 120 psig of ethylene. The autoclave was stirred
4 at 50° for 30 minutes, then cooled and vented. The contents were
5 dried under a stream of air. The weight of the polymer isolated
6 was 44.7 g. The melting point of the polymer was 117°C and
7 analysis by infra-red spectroscopy indicated that there were about
8 17 ethyl branches per 1000 carbon atoms.

9 EXAMPLE 24

10 In this example, ethylene and 1-butene were copolymerized
11 in a toluene diluent by adding under a nitrogen atmosphere to a 1
12 liter stainless-steel autoclave, previously flushed with nitrogen
13 and containing 400 ml of dry, oxygen-free toluene, 50 ml of a
14 catalyst solution in toluene containing 70 mg of bis(cyclopenta-
15 dienyl)hafnium dimethyl and 45 mg of N,N-dimethylanilinium
16 bis(7,8-dicarbaundecaborato)cobaltate(III). 1-Butene (200 ml) was
17 added to the autoclave, which was further pressurized with 120 psig
18 of ethylene. The autoclave was stirred at 50° for 20 minutes, then
19 cooled and vented. The contents were dried under a stream of air.
20 The yield of isolated polymer was 75.1 g. The melting point of the
21 polymer was 109°C and analysis by infra-red spectroscopy indicated
22 that there were about 29 ethyl branches per 1000 carbon atoms.

23 EXAMPLE 25

24 In this example, ethylene was polymerized by reacting 66
25 mg of 1-bis(cyclopentadienyl)titana-3-dimethylsilacyclobutane and
26 88 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
27 cobaltate(III) in 25 ml of toluene in a serum-capped round-bottomed
28 flask. The solution darkened on passage of ethylene through it.
29 After 10 minutes, the flask was opened and the contents diluted
30 with ethanol. The polymer was filtered off, washed with ethanol
31 and acetone, and dried. The yield of polyethylene isolated was
32 0.09 g.

33 EXAMPLE 26

34 In this example, ethylene was polymerized by reacting 61
35 mg of 1-bis(cyclopentadienyl)zircona-3-dimethylsilacyclobutane and
36 87 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
37 cobaltate(III) in 20 ml of toluene in a serum-capped round-bottomed

1 flask. On passing ethylene through the solution, polymer
2 precipitated as the solution grew warm. After 10 minutes, the vial
3 was opened and the contents diluted with ethanol. The precipitate
4 was filtered off, washed with ethanol, and dried. The yield of
5 polyethylene isolated was 1.41 g.

6 EXAMPLE 27

7 In this example, ethylene was polymerized by reacting 82
8 mg of 1-bis(cyclopentadienyl)hafna-3-dimethylsilacyclobutane and 88
9 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
10 cobaltate(III) in 20 ml of toluene in a serum-capped round-bottomed
11 flask. On passing ethylene through the solution, polymer
12 precipitated as the solution grew hot. After 5 minutes, the flask
13 was opened and the contents diluted with ethanol. The polymer was
14 filtered off, washed with ethanol, and dried. The yield of
15 polyethylene isolated was 1.54 g.

16 EXAMPLE 28

17 In this example, ethylene was polymerized by reacting 67
18 mg of bis(cyclopentadienyl)zirconium(2,3-dimethyl-1,3-butadiene)
19 and 88 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
20 cobaltate(III) in 50 ml of toluene in a serum-capped bottle.
21 Ethylene was passed through the solution, which gradually grew
22 warm. After 15 minutes, the bottle was opened and the contents
23 diluted with ethanol. The polymer was filtered off, washed with
24 ethanol, and dried. The yield of polymer isolated was 1.67 g.

25 EXAMPLE 29

26 In this example, ethylene was polymerized by reacting 40
27 mg of bis(cyclopentadienyl)hafnium(2,3-dimethyl-1,3-butadiene) with
28 43 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)
29 cobaltate(III) in 50 ml of toluene in a serum-capped bottle.
30 Ethylene was passed through the solution, which became turbid
31 within 30 seconds. After 20 minutes, the bottle was opened and the
32 contents diluted with ethanol. The solid polymer was filtered off,
33 washed with ethanol, and dried. The yield of polyethylene isolated
34 was 0.43 g.

35 EXAMPLE 30

36 In this example, ethylene was polymerized by reacting 55
37 mg of (pentamethylcyclopentadienyl)(tetramethyl-eta¹-methylene

1 -eta⁵-cyclopentadienyl)zirconium phenyl and 45 mg of N,N-di-
2 methylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III) in 20 ml
3 of toluene in a serum-capped round-bottomed flask. On passing
4 ethylene through the solution, polymer formed almost instantly and
5 much heat was evolved. After 5 minutes, the flask was opened and
6 the contents diluted with ethanol. The precipitate was filtered
7 off, washed with acetone, and dried. The yield of polyethylene
8 isolated was 0.55 g.

9 EXAMPLE 31

10 In this example, ethylene was polymerized by reacting 80
11 mg of (pentamethylcyclopentadienyl)(tetramethylcyclopentadienyl-
12 methylene)hafnium benzyl and 60 mg of N,N-dimethylanilinium
13 bis(7,8-dicarbaundecaborato)cobaltate(III) in 50 ml of toluene in a
14 serum-capped bottle. Ethylene was passed through the solution for
15 10 minutes. Polymer precipitated as the solution grew warm. The
16 bottle was opened and the contents diluted with ethanol. The solid
17 polymer was filtered off, washed with acetone, and dried. The
18 yield of polyethylene isolated was 0.92 g.

19 EXAMPLE 32

20 In this example, ethylene was polymerized by reacting 0.42
21 g of bis(trimethylsilylcyclopentadienyl)hafnium dimethyl with 0.08
22 g N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III)
23 in 10 ml of toluene. A portion of this solution (0.4 ml) was
24 injected under a pressure of 3000 bar of Isopar into an autoclave
25 pressurized to 1500 bar with ethylene and heated to 160°. After 5
26 seconds the contents of the autoclave were discharged. Linear
27 polyethylene (2.1 g) with a weight-average molecular weight of
28 144,000 and a molecular weight distribution of 2.9 was isolated.

29 While the present invention has been described and
30 illustrated by reference to particular embodiments thereof, it will
31 be appreciated by those of ordinary skill in the art that the same
32 lends itself to variations not necessarily illustrated herein. For
33 this reason, then, reference should be made solely to the appended
34 claims for purposes of determining the true scope of the present
35 invention.

CLAIMS:

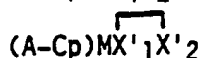
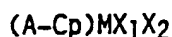
1. Method for preparing a catalyst comprising the steps of:

(a) combining, in a suitable solvent or diluent, at least one first compound consisting of a bis(cyclopentadienyl)metal compound containing at least one substituent capable of reacting with a proton, said metal being selected from the group consisting of titanium, zirconium and hafnium and at least one second compound comprising a cation, capable of donating a proton, and an anion containing a plurality of boron atoms which is bulky, labile and capable of stabilizing the metal cation formed as a result of the reaction between the two compounds;

(b) maintaining the contacting in step (a) for a sufficient period of time to permit the proton provided by the cation of said second compound to react with said substituent contained in said metal compound; and

(c) recovering an active catalyst as a direct product or as a decomposition product of one or more of said direct products from Step (b).

2. Method according to Claim 1 wherein said bis(cyclopentadienyl)metal compound may be represented by the following general formulae:

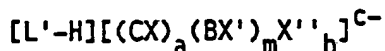


Wherein:

M is a metal selected from the group consisting of titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals, optionally two independently substituted or unsubstituted radicals; A' is a covalent bridging group

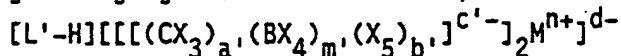
containing a Group IV-A element; L is an olefin, diolefin or aryne ligand; X_1 and X_2 are, independently, selected from the group consisting of hydride radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, optionally two lower alkyl substituents or two hydrides, organo-metalloid radicals and the like; X'_1 and X'_2 are joined and bound to the metal atom to form a metallacycle, in which the metal, X'_1 and X'_2 form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and R is a substituent on one of the cyclopentadienyl radicals which is also bound to the metal atom.

3. Method according to Claim 1 or Claim 2 wherein said second compound may be represented by one of the following general formulae:



Wherein:

$L'-H$ is either H^+ , ammonium or a substituted ammonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B and C are, respectively, boron and carbon; X, X' and X'' are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; a and b are integers ≥ 0 ; c is an integer ≥ 1 ; $a + b + c =$ an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22; and/or



Wherein:

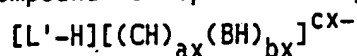
$L'-H$ is either H^+ , ammonium or a substituted-ammonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up

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to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, M and H are, respectively, boron, carbon, a transition metal and hydrogen; X_3 , X_4 and X_5 are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; a' and b' are the same or a different integer ≥ 0 ; c' is an integer ≥ 2 ; $a + b' + c' =$ an even-numbered integer from 4 to about 8; m' is an integer from 6 to about 12; n is an integer such that $2c' - n = d$; and d is an integer ≥ 1 .

4. Method according to any of the preceding claims wherein the contacting of step (a) is accomplished at a temperature within the range from about -100°C to about 300°C , preferably at from 0 to 45,000 psig.

5. Method according to any of the preceding claims wherein said second compound is represented by the general formula:



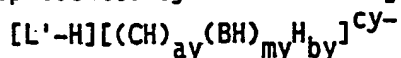
Wherein:

$L'-H$ is either H^+ , ammonium or a substituted-ammonium optionally tri-substituted radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, and H are, respectively, boron, carbon and hydrogen; ax is either 0 or 1; cx is either 2 or 1; $ax + cx = 2$; and bx is an integer ranging from 10 to 12.

6. Method according to Claim 6 wherein said second compound is selected from the group consisting of bis[tri(n-butyl) ammonium] dodecaborate and tri(n-butyl)ammonium 1-carbaundeca or 1-carbadodecaborate and said first compound is selected from the group consisting of bis(pentamethylcyclopentadienyl)zirconium

dimethyl, (pentamethylcyclopentadienyl) (cyclopentadienyl)zirconium dimethyl, and [1,3-bis(trimethylsilyl)cyclopentadienyl]zirconium dimethyl.

7. Method according to any of Claims 1 to 4 wherein said second compound is represented by the following general formula:

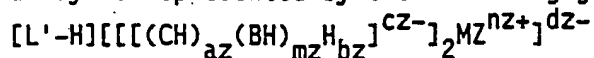


Wherein:

L'-H is either H⁺, ammonium or a substituted-ammonium, optionally tri-substituted, radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C and H are, respectively, boron, carbon and hydrogen; ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3; ay + by + cy = 4; and mx is an integer from 9 to 18.

8. Method according to Claim 7 wherein said second compound is selected from the group consisting of tri(n-butyl) ammonium 7,8-dicarbaundecaborate and tri(n-butyl)ammonium tridecahydrido-7-carbaundecaborate in which case preferably the first compound is bis(pentamethylcyclopentadienyl)zirconium dimethyl and/or wherein L'-H is H⁺, preferably 7,8-dicarbaundecaborane(13) or octadecaborane(22) in which case optionally said first compound is selected from the group consisting of bis(pentamethylcyclopentadienyl)zirconium dimethyl and bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl.

9. Method according to any of Claims 1 to 4 wherein said second compound may be represented by the following general formula:



Wherein:

L'-H is either H⁺, ammonium or a substituted ammonium radical having up to 3 hydrogen atoms replaced with a

hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, H and MZ are, respectively, boron, carbon, hydrogen and a transition metal; az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from 9 to 11; $az + bz + cz = 4$; and nz and dz are, respectively, 2 & 2 or 3 & 1.

10. Method according to Claim 9 wherein said second compound is N,N-dimethylanilinium bis(undecahydrido-7,8-dicarbaundecaborato) cobaltate(III) and/or wherein said first compound is selected from the group consisting of 1-bis(cyclopentadienyl)titana-3-dimethylsilacyclobutane, 1-bis(cyclopentadienyl)zircona-3-dimethylsilacyclobutane, and 1-bis(cyclopentadienyl)hafna-3-dimethylsilacyclobutane, bis(cyclopentadienyl) zirconium (2,3-dimethyl-1,3-butadiene) and bis(cyclopentadienyl) hafnium(2,3-dimethyl-1,3-butadiene), (pentamethylcyclopentadienyl) (tetramethylcyclopentadienyl-methylene)zirconium phenyl and (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylene) hafnium benzyl; or wherein said second compound is selected from the group consisting of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)nickelate(III) and N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) ferrate(III) in which case preferably said first compound is bis(pentamethylcyclopentadienyl)zirconium dimethyl.

11. Method for polymerizing an α -olefin, a diolefin and/or an acetylenically unsaturated compound containing from 2 to about 18 carbon atoms either alone or in combination with one or more other monomers comprising the steps of:

(a) contacting at a temperature within the range from about -100°C to about 300°C and at a pressure within the range from about 0 to about 45,000 psig. an olefin, diolefin and/or an acetylenically unsaturated monomer either alone or in combination with one or more other monomers in a suitable

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carrier, solvent or diluent with a catalyst prepared previously or in situ during polymerization by a method according to any of the preceding claims;

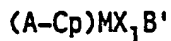
(b) continuing the contacting of step (a) for a sufficient period of time to polymerize at least a portion of said olefin;

(c) recovering a polymer product.

12. A catalyst prepared by a method according to any of Claims 1 to 10.

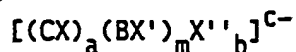
13. Polyolefin produced in accordance with the method of claim 11.

14. Composition of matter containing compounds represented by the following general formula:



Wherein:

M is a metal selected from the group consisting of titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either (Cp)(Cp*) or CP-A'-Cp* and Cp and Cp* are the same or different substituted or unsubstituted cyclopentadienyl radicals; A' is a covalent bridging group containing a Group IV-A element; X₁ is selected from the group consisting of hydride radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; and B' is a compatible non-coordinating anion which may be represented by one of the following general formulae:

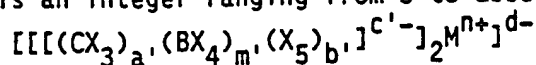


Wherein:

B and C are, respectively, boron and carbon; X, X' and X'' are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; a and b are integers ≥ 0 ; c is an integer ≥ 1 ;

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$a + b + c =$ an even-numbered integer from 2 to about 8;
and m is an integer ranging from 5 to about 22; and 34



Wherein:

B , C and M are, respectively, boron, carbon and a transition metal; X_3 , X_4 and X_5 are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; a' and b' are the same or a different integer ≥ 0 ; c' is an integer ≥ 2 ; $a' + b' + c' =$ an even-numbered integer from 4 to about 8; m' is an integer from 6 to about 12; n is an integer such that $2c' - n = d$; and d is an integer ≥ 1 .

15. Composition of matter according to Claim 14 wherein (A-Cp) is a bis(peralkyl-substituted cyclopentadienyl); X is an alkyl group; B' is (dodecahydrido-7,8-dicarbaundecaborato) and M is zirconium and wherein each of the alkyl groups in the peralkyl-substituted cyclopentadienyl radicals are, independently, C_1 - C_{20} alkyl radicals and the alkyl group is a C_1 - C_{20} alkyl radical, the peralkyl substitution being preferably pentamethyl or ethyltetramethyl and the alkyl radical being preferably a methyl radical.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 88/00222

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 08 F 4/64; C 08 F 4/76; C 08 F 10/00; C 07 F 17/00														
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 25%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">C 08 F; C 07 F</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	C 08 F; C 07 F								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; padding: 5px;">Category ⁹</th> <th style="width: 70%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Journal of the Chemical Society, Chemical Communications, 1986, M. Bochmann et al.: "Synthesis and insertion reactions of cationic alkylbis(cyclopentadienyl)titanium complexes", pages 1610-1611 see the whole abstract cited in the application --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0200351 (MITSUI PETROCHEM) 5 November 1986 see the whole document cited in the application --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 3231593 (W. HAFNER et al.) 25 January 1966 see claims; column 5, line 71 - column 7, line 7; examples -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	Journal of the Chemical Society, Chemical Communications, 1986, M. Bochmann et al.: "Synthesis and insertion reactions of cationic alkylbis(cyclopentadienyl)titanium complexes", pages 1610-1611 see the whole abstract cited in the application --	1	A	EP, A, 0200351 (MITSUI PETROCHEM) 5 November 1986 see the whole document cited in the application --	1	A	US, A, 3231593 (W. HAFNER et al.) 25 January 1966 see claims; column 5, line 71 - column 7, line 7; examples -----	1
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; margin-top: 10px;">14th April 1988</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">19 MAY 1988</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> </td> <td style="padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> P.C.G. VAN DER PUTTEN </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; margin-top: 10px;">14th April 1988</div>	Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">19 MAY 1988</div>	International Searching Authority <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> P.C.G. VAN DER PUTTEN </div>								
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8800222

SA 20798

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/05/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0200351	05-11-86	JP-A- 61221207	01-10-86
		US-A- 4704491	03-11-87
		JP-A- 62121710	03-06-87
<hr/>			
US-A- 3231593		None	
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